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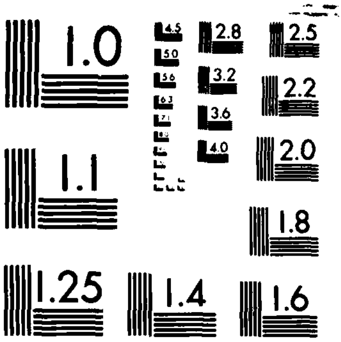

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When phenylacetylene plus tungsten hexachloride initiate the metathesis of cyclopentene, poly(phenylacetylene) is found attached to the resulting polypentenamer chains. The average amount of this poly(phenylacetylene) does not vary as the growth of the polypentenamer chains is checked by added diphenylacetylene, showing it to be present as a block at their start. The implication is that the metathesis is initiated by the growing acetylene

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uniting with the olefin, strong evidence for the hypothesis that the acetylene polymerization is propagated by metal-carbenes.

The variations that occur in the length of the chains and the amount of poly(phenylacetylene) attached to the average chain as the acetylene concentration is varied are analyzed for the underlying kinetic parameters. The stabilized metal-carbenes propagating the phenylacetylene polymerization react 3 x 10^3 times more quickly with phenylacetylene than with cyclopentene, whereas the less stabilized metal-carbenes propagating the cyclopentene metathesis select 17-fold in the opposite direction. Diphenylacetylene is 26 times more effective than phenylacetylene in quenching the metathesis, and 2.4 times more effective than phenylmethylacetylene. The key to the experiments is the observation that diphenylacetylene in minute amounts quenches metathesis but does not initiate the reaction.

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A Procedure Identifying a Polyacetylene Initiator of Olefin Metathesis. The Reactivities of Metal-Carbenes Toward Alkenes and Alkynes

by

Chien-Chung Han and Thomas J. Katz

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A Procedure Identifying a Polyacetylene Initiator of Olefin Metathesis. The Reactivities of Metal-Carbenes Toward Alkenes and Alkynes

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Contribution from the Department of Chemistry,

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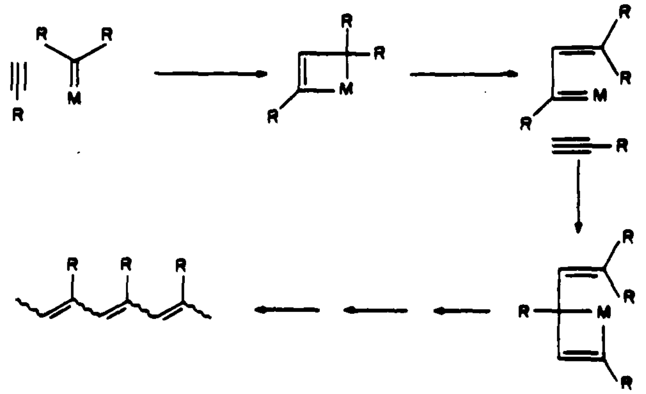
Abstract: When phenylacetylene plus tungsten hexachloride initiate the metathesis of cyclopentene, poly(phenylacetylene) is found attached to the resulting polypentenamer chains. The average amount of this poly(phenylacetylene) does not vary as the growth of the polypentenamer chains is checked by added diphenylacetylene, showing it to be present as a block at their start. The implication is that the metathesis is initiated by the growing acetylene uniting with the olefin, strong evidence for the hypothesis that the acetylene polymerization is propagated by metal-carbenes.

The variations that occur in the length of the chains and the amount of poly(phenylacetylene) attached to the average chain as the acetylene concentration is varied are analyzed for the underlying kinetic parameters. The stabilized metal-carbenes propagating the phenylacetylene polymerization react 3×10^3 times more quickly with phenylacetylene than with cyclopentene, whereas the less stabilized metal-carbenes propagating the cyclopentene metathesis select 17-fold in the opposite direction. Diphenylacetylene is 26 times more effective than phenylacetylene in quenching the metathesis, and 2.4 times more effective than phenylmethylacetylene. The key to the experiments is the observation that diphenylacetylene in minute amounts quenches metathesis but does not initiate the reaction.

Introduction

The hypothesis that the metal-catalyzed polymerization of acetylenes,[1] like the olefin metathesis reaction,[2] proceeds by metal-carbenes adding to unsaturated linkages and subtracting from the resulting four-membered rings,[3,4] (Scheme I) suggests that if a metal-derivative initiates the polymerization of an acetylene, the acetylene might induce the metal derivative to metathesize olefins (Scheme II).[5] In the presence of an olefin the metal-carbenes that supposedly propagate the acetylene polymerization might add to this acetylene-surrogate instead. The observation of products characteristic of olefin metathesis would thus provide a way to detect the presence of otherwise invisible metal-carbenes.

Scheme I



Scheme II

olefin + metal-derivative → no metathesis

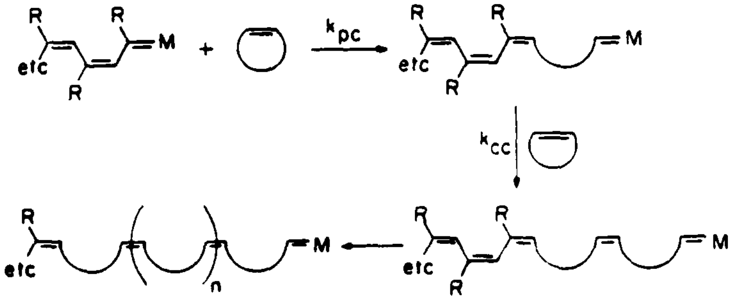
metal-derivative + acetylene → polyacetylene

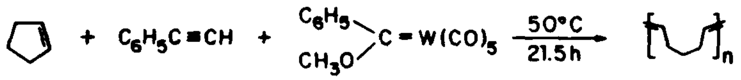
olefin + metal-derivative + acetylene → metathesis!

Scheme II would also be the basis for an interesting way to initiate olefin metatheses. Indeed there are two successful tests of the scheme, experiments showing that metatheses are induced by combinations of phenylacetylene either with the Fischer metal-carbene pentacarbonyl(methoxyphenylmethylene)-tungsten[5a-c] or with tungsten hexachloride.[5d,6] However, since these experiments do not exclude alternative mechanisms by which the combinations might, possibly, induce the metatheses, other evidence was sought that would bear on the hypothesis.

The following more stringent test was therefore designed: since the initiator of olefin metathesis in these combinations is supposed to be the growing polyacetylene, if the olefin employed were cyclic, a polyacetylene fragment would have to be found attached to every polyalkenamer [or poly-(1-alkene-1,ω-diyl), in chemical abstracts nomenclature], at the initiating end of the chain (Scheme III). To detect this fragment, samples of polymer formed according to equation 1 (here x varied between 0.3 and 3.0) were dispersed by gel permeation chromatography and analyzed both by their refractive index (RI), which detects the bulk of the polymer, essentially all polypentenamer, and by their light absorption, which detects red

Scheme III





(1)

100 : $0.3 \leq x \leq 3$: 1

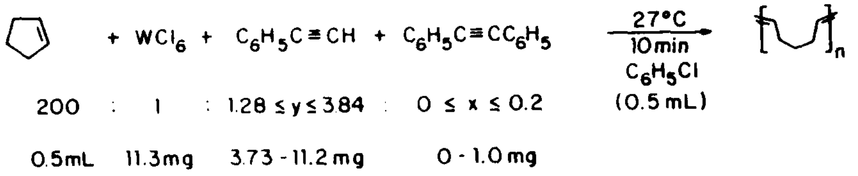
poly(phenylacetylene) units.[5c,7] The result was that the analyses by light-absorption detected two polymer distributions, one at low molecular weight (ca. 10^4 g/mol) corresponding to poly(phenylacetylene) that terminated without initiating the formation of polypentenamer chains, and one at high molecular weight (> 10^5 g/mol) that paralleled the bulk of the polymer as detected by the refractive index monitor and that presumably arises from the polyacetylene fragment of the metal-carbene that initiated the growth of the polyalkenamer.[5c] These experiments could not however show whether the chromophores accounting for the high molecular weight absorption were localized at the initiating end of the polyalkenamer chains, or whether they were impurities, possibly formed in minor side reactions such as occasional oxidation of alkenamer units.

The experiments reported in this paper, which made use of polymers formed according to the related procedure summarized in equation 2,[5d] show

(2)

200 $0.3 \leq y \leq 4$: 1

that the light-absorbing units are not attached randomly along the polymers, but are attached as a block at their origins. They also show that the amount of the chromophore increases as the concentration of phenylacetylene in the reaction mixture increases. The experiments thus serve to identify the light-absorber as the polyacetylene in Scheme III. The sizes of the blocks and the sizes of the polymers are analyzed for the underlying kinetic parameters. The peculiar fact is also reported that although di phenylacetylene does not initiate metatheses of cyclopentene, it is superbly effective in quenching them. It is this discovery that is the key to identifying the initiating polyacetylene block, for if one considers experiments like those summarized in equation 3, the effect of increasing amounts of disubstituted acetylene is to shorten the polymer chains without affecting their initiation. The section below demonstrates and analyzes this effect.



(3)

Results

Quenching and Initiation of Polypentenamer Chains. Figure 1 illustrates how effective trace amounts of diphenylacetylene, even 0.1 mg/mL, are in quenching the yields of polypentenamer that form in equation 3. Figure 2 shows that the mechanism involves quenching the growth of the polymer chains, not interfering with their initiation (this point is elaborated below), for the inverse of the number average molecular weight of the polypentenamers varies linearly with the concentration of the diphenylacetylene.[9,10] For the experiments summarized in figure 2, the number of equivalents of phenylacetylene (y in equation 3) was 1.28, and the slope of the linear correlation was measured by the method of least squares as $(1.17 \pm 0.11) \times 10^2$. In similar experiments, in which 2.56 equivalents were used, the results were similar. The slope was $(1.10 \pm 0.04) \times 10^2$, and the average for the two kinds of experiments was then $(1.14 \pm 0.07) \times 10^2$. It will be shown below that for these experiments to succeed, the amount of phenylacetylene must be about 2.5 equivalents or less if 0.2 equivalents or less of diphenylacetylene are to quench an appreciable fraction of the chains. If the amount is much more, the diphenylacetylene can not compete with the phenylacetylene.

That this ability of diphenylacetylene to stop the growth of polypentenamer chains is not matched by an ability to initiate them is demonstrated by experiments measuring how the number of chains varies with the concentration of diphenylacetylene. The number of polypentenamer chains created in each experiment in equation 3 is the ratio of the weight of the polypentenamer that forms and its number average molecular weight. However, as elaborated in the Discussion Section, a more accurate measure should be obtained by following the procedure summarized in figure 3. This shows, for assorted values of y in equation 3, how the total weight of polymer varies with the number average molecular weight of the polypentenamer as the amount of diphenylacetylene (x) is changed, the linearity implying that the number of polypentenamer chains, N_c, the slope, is not dependent on the diphenylacetylene concentration.

That diphenylacetylene does not appreciably induce tungsten hexachloride to initiate cyclopentene's polymerization was also tested directly by combining tungsten hexachloride with 200 equivalents of cyclopentene in 0.5 mL of chlorobenzene and amounts of diphenylacetylene that were distributed in ten trials between 0.01 and 10 equivalents. The yield of polymer in all these experiments was, after 10 minutes at 27 °C, never more than 0.7 %.

Identification of the Initiating Block. Figure 4 illustrates how the gel permeation chromatograms of the polymers formed in equation 3 vary as the amount of diphenylacetylene (x) is changed. Three points discussed in the Introduction Section are evident in this figure. One is that the molecular weight distribution is bimodal, due presumably to UV absorbing poly(phenylacetylene) at low molecular weight that is not attached to polypentenamer and at high molecular weight that is attached. Another is that the molecular weights of the polypentenamers decrease as the amount of diphenylacetylene increases. (The curves centered at high molecular weights move to the right.) And last, the intensity of the UV absorption parallels the RI response, as expected if the absorbing species and the polypentenamer chains are attached.

However, the chromatograms exhibit two additional features demonstrating that the light absorbers are not distributed randomly along the polypentenamer chains, but are localized at their beginnings. The first is that the intensity of the UV absorption increases in relation to the RI difference as the amount of diphenylacetylene increases. With increased diphenylacetylene concentration, the polypentenamer chains are cut shorter. If the UV absorption were caused by randomly oxidized units on the chain, or indeed by any UV absorbing species associated with the bulk of the polymer, the UV absorption intensity per chain would decrease just as the RI intensity per chain decreases. The UV intensity per unit weight, and therefore the ratio of the UV and RI intensities, would not vary. But if the chromophores are, as expected according to the hypothesis in Scheme III, at the origin of each polypentenamer, their amount would not decrease as the chains are shortened. The UV absorption per unit weight of sample would increase, and the ratio of the UV and RI intensities would rise. This is what is observed.

There is a quantitative test of this analysis. If the UV absorption is associated with an initiating block, although the intensity of absorption per unit weight of sample increases as the growth of the polymer chains is checked, the intensity of absorption for the whole polypentenamer sample should remain unchanged. That this is so is shown in figure 5, which displays, as a function of the number of equivalents of diphenylacetylene in equation 3, the integrated UV absorption intensities under the high molecular weight gel permeation chromatographic peaks summed over whole samples and labeled (using the measured absorption intensity per unit weight) as milligrams of poly(phenylacetylene). This integrated intensity is independent of the diphenylacetylene concentration for three series of experiments in which the amounts of phenylacetylene used (y in equation 3) were 1.28, 2.56, and 3.84. Thus the total amount of the UV absorbing species remains constant while the molecular weight decreases that is associated with it (as measured by the high molecular weight UV peak in figure 4) and with the polypentenamer (as measured by the RI peak in figure 5). It would be hard to explain if each polyacetylene block were not attached to the start of a polypentenamer chain.

Figure 5 also shows that the total UV absorption associated with the high molecular weight peak rises with the concentration of phenylacetylene, and it will be shown below (Figure 7) that this is not just because the phenylacetylene increases the number of chains (Figure 9), but because as the concentration increases, the average size of the initiating block on each chain also increases. Accordingly, it is unlikely that the UV absorption was mistakenly associated with poly(phenylacetylene) when it should have been associated with an initiating tungsten moiety, for its size per chain would not have increased.

The second feature of the chromatograms in figure 4 that locates the poly(phenylacetylene) units at the start of the polypentenamer chains is the displacement of the UV peaks to the right of the refractive index peaks. If a poly(phenylacetylene) block begins each polypentenamer chain, the intensity of the UV absorption due to that block, and therefore to the chain, will be independent of the chain's length. Even if there is a distribution in the size of initiating blocks, the average absorption per chain will not depend on the chain's length. It follows that the UV absorptions (but not the RI intensities) per unit mass will be greater for smaller polypentenamers than for larger ones, and the UV peaks will consequently shift to the right of the RI peaks.

This effect, first recognized by Kennedy *et al.*, and applied to analyze polyisobutylene that contained a known initiator fragment and known end groups,[15] can be evaluated quantitatively. Following Kennedy, figure 6 displays the ratio of the intensity recorded by the UV and RI monitors at the UV peak maximum divided by this ratio at various elution times, x, as a function of the ratio of the molecular weights of polypentenamer eluted at times x and at the peak maximum. The function should be linear, have slope one, and pass through the origin.[16]

An alternative analysis compares molecular weight averages calculated assuming intensities in gel permeation chromatograms are proportional to mass with those assuming intensities are proportional to chain number, for in the experiments reported here, the refractive index monitor should

Experimental Section

Materials. Cyclopentene (from Aldrich Chemical Co.) was stirred with a small amount of N-phenyltriazolinedione at ambient temperature for ca. 1/2 h to remove cyclopentadiene, then decanted from a precipitate, and distilled through a spinning band column. A center fraction, after redistillation from CaH_2 through a Vigreaux column, was measured to be 99.96 % pure by gas chromatography (gc) analysis (glass column, 2 mm x 6', 10 % OV17 on 80 - 100 mesh chromosorb Q) at 32 °C. Diphenylacetylene ("99 %" from Aldrich) was recrystallized twice from ethanol, and dried at 0.4 torr (room temperature overnight, 50 °C for 2 h). Mp = 60.5 - 62.5 °C (reported:[30] ca. 61 °C). Phenylacetylene (">99 % pure" from Aldrich) was distilled at 90 torr through the spinning band column and analyzed as 99.6 % pure by gc (1/8" x 10' 3 % carbowax 20 M on chromosorb W-AW/DCMS) at 90 °C. WCl_6 (from Pressure Chemical Co.) was purified before each experiment by subliming away $WOCl_4$ in an N_2 stream at 120 °C. Chlorobenzene (Fischer Scientific) was washed repeatedly with concd. H_2SO_4 until yellow color was no longer extracted, dried (KOH), and distilled from CaH_2. The tetrahydrofuran (THF) for the gel permeation chromatographic analyses was distilled from anhydrous Cu_2Cl_2 to remove peroxides and antioxidants.[31]

Polymerization of Cyclopentene. Phenylacetylene (111.8 mg) was dissolved in cyclopentene (15 mL), and diphenylacetylene (10.2 mg) was added to a 5 mL portion. These two solutions were combined to prepare others containing lesser amounts of diphenylacetylene. To 0.5 mL portions of these solutions in 3.5 mL screw capped vials (containing air) there was added 0.5 mL portions of a solution of 225.8 mg WCl_6 in 10 mL of chlorobenzene. After

The Role of Diphenylacetylene. If the experiment with diphenylacetylene had not been performed, the rate data could still have been derived. Indeed, if only those experiments described by equation 3 are considered in which no diphenylacetylene is present, the rate constant ratios measured are essentially similar to the more precise measurements that use all the data. The graph of the inverse of the number average molecular weight of the polypentenamer formed in the reaction is linearly proportional to the phenylacetylene concentration, and the slope implies that $k_{cp}/k_{cc} = 0.063 \pm 0.005$, only 7 % different from the value in Table III. Similarly, a graph of the inverse of the number average molecular weight of the poly(phenylacetylene) attached to the high molecular weight chain is linearly proportional to the inverse of the phenylacetylene concentration used to prepare the polymer (as in figure 8), and the slope implies that $k_{pp}/k_{pc} = (2.9 \pm 0.5) \times 10^3$, identical with the value in Table III. For this last analysis the molecular weight of the poly(phenylacetylene) block could not be derived by the procedure in figure 7, but was determined by multiplying the amount of phenylacetylene attached to each gram of polypentenamer, as measured by the UV peak in the gel permeation chromatogram, and the number average molecular weight of the high molecular weight chain.

The role of the diphenylacetylene in the experiments above is thus not a critical one in the quantitative analysis. It is, however, critical to the greater task of demonstrating how the phenylacetylene induces cyclopentene to polymerize and how the phenylacetylene polymerization works, for it is only the experiments performed with it that demonstrate that the light-absorbing material is attached to the polypentenamer at the initiating end. This demonstration strongly supports the hypothesis that the acetylene polymerization is an olefin metathesis.

as their gel permeation chromatography peaks overlap with the peaks of poly(phenylacetylene). The slopes are then higher by about 60 %, and in the analogue of figure 9, the linear correlation is worse and the slope higher (by 73 %). It is important to note that although we therefore believe that figures 3 and 9 treat the experimental data correctly, the slopes in these figures are parameters neither in the derivation of the rate constant ratios in Table III nor in the analyses implying that poly(phenylacetylene) is attached at the origin of the polypentenamer chains.

$\bar{M}_n$ for Attached and Unattached Poly(phenylacetylene). The mechanism envisioned for the initiation of metathesis would have metal-carbenes P_n that usually add additional phenylacetylene units (Equation 7) occasionally choosing to add to a cyclopentene unit instead (Scheme III). The choice however should be independent of n, the degree of polymerization of the phenylacetylene. This would mean that the number average molecular weights of the poly(phenylacetylene) that is attached to the polypentenamer and the poly(phenylacetylene) that is unattached should be the same. The data in Table I support this hypothesis, but the evidence has to be interpreted in light of the experimental problems involved in collecting free poly(phenylacetylene), especially that of low molecular weight, whose loss will increase the average molecular weight measured. Also, possible differences (discussed above) between the structure of the poly(phenylacetylene) made here and that used to calibrate the gel permeation chromatograms (see Table I and reference 18) could alter the "corrected molecular weights" in the Table.

Initiation of Phenylacetylene's Polymerization. The experiments also give information about the reaction by which the polymerization of phenylacetylene is initiated. Thus while the number of polypentenamer chains (N_c) formed in equation 3 is seen in figure 3 not to depend on the concentration of diphenylacetylene, it does depend on the concentration of phenylacetylene. Figure 9 shows that this dependence appears to be linear, implying that the chain initiation reaction varies with the first power of the phenylacetylene concentration. The result contrasts with the previous observation that the rates at which similar polymerizations are initiated by pentacarbonyl(methoxyphenylmethylene)tungsten are independent of the phenylacetylene concentration.[5c] (Presumably in this case a rate-determining loss of carbon monoxide precedes the interaction of the metal-carbene with the acetylene.[27]) Both the present and previous results accord with reports on the rates of phenylacetylene polymerization initiated by the metal-carbene[28] and by $MoCl_5$ (data for WCl_6 are not available),[29] inasmuch as the reaction order in phenylacetylene concentration is one higher for the latter than for the former (1 versus 0).

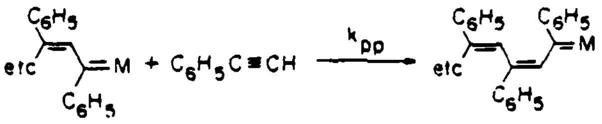
The virtue of measuring the number of chains for figure 9 using the plots in figure 3 is that account can be taken of what the weight of the polymer would be if the number average molecular weight of the polypentenamer were zero, and we chose for this weight 30 % of the phenylacetylene used in the experiments. The exact figure is not critical (the analyses of residual phenylacetylene imply it may be as high as 69%), but it should reasonably be small and positive. If account is <u>not</u> taken of this point, the intercepts are slightly negative, probably in part because low molecular weight polymer does not all precipitate and because the accuracy with which the molecular weights of small polypentenamers can be measured is diminished

Table III here

Systematic errors that add to the random errors estimated in Table III to degrade the precision of the rate constant ratios include errors correcting for the consumption of phenylacetylene as well as possible fluctuations in the extinction coefficient of poly(phenylacetylene) resulting from changes in its structure. With respect to the latter, the structure of poly(phenylacetylene is known to depend on the initiator used,[3,23] the polymerization solvent,[23c,d,24] and the thermal history of the sample,[23a,b,25] but when the extinction coefficients at 254 nm are compared of various samples of differing detailed structure, prepared using different catalysts and solvents, the range is only 14 %.[3,26] Comparing the extinction coefficients reported for samples prepared in methylene chloride[3] with those measured here for samples prepared in chlorobenzene (the initiator for both sets was WCl_6), the difference is 33 %. Thus the errors associated with the values of k_{pp}/k_{pc} are likely to be two or three times the random errors recorded in Table III. However the essential point, that k_{pp} is ca. 3000 times k_{pc}, should still be valid.

The rate constant ratios reported here are remarkably similar to the analogous rate constant ratios derived from preliminary data reported earlier for the reactions in equation 1, in which the initiator was the Fischer metal-carbene.[5c] The comparison is also recorded in Table III, the rate constant ratios there having been derived from the data in the earlier paper by the procedures reported here, which we believe more likely to be correct than those used before.

k_{pp}/k_{pc} is, when k_{pp} is the second order rate constant for the reaction propagating the polymerization of the acetylene (equation 7) and k_{pc} is the rate constant defined in Scheme III for the reaction that terminates it. Equivalently for the experiments in equation 3, the slope of the line in figure 8 (multiplied, as discussed above, by 1.52, the factor to correct for phenylacetylene consumed) implies that $k_{pp}/k_{pc} = (2.9 \pm 0.4) \times 10^3$. This means



P_n P_{n+1} (7)

that only very rarely does the growing poly(phenylacetylene initiate the polymerization of cyclopentene. However when it does, the metal-alkylcarbene quickly adds another 500 - 3,500 cyclopentene units before (under the conditions of equation 3) its growth is quenched.

The rate data are summarized in Table III. Notable is the observation that the metal-carbenes propagating the polymerization of phenylacetylene (Equation 7) are much more selective in choosing phenylacetylene or cyclopentene as their reaction partners than are the metal-carbenes propagating the cyclopentene metathesis. Also notable is the change in the direction of this choice, since the former metal-carbenes (the P_n's) select the acetylene over the alkene, while the latter (the C_n's) choose oppositely.[22] The greater selectivity of metal-carbene P_n compared to metal-carbene C_n might reflect the effects of substituent groups, especially unsaturated ones, in sterically and electronically attenuating the reactivities of metal-carbenes, but the reasons for the change in the direction of the selection are not evident.

could be analyzed in the same way as that by diphenylacetylene. The data for $y = 1.28$ shows that if k_{cm} is the rate constant for this acetylene analogous to k_{cd}, then $k_{cm}/k_{cc} = 0.646 \pm 0.04$. Thus $k_{cm} = 0.42\ k_{cd}$ (the phenylmethylacetylene is only 42 % as reactive as the diphenylacetylene), but $k_{cm} = 11\ k_{cp}$, meaning that phenylmethylacetylene is much more reactive than phenylacetylene. Thus there is a perfect inverse ordering of the ability of all three acetylenes to quench the metatheses (diphenyl > phenylmethyl > phenyl) and of their reactivity toward polymerization induced by WCl_6 plus $(C_6H_5)_4Sn$ (phenyl >> phenylmethyl > diphenyl)![19] The high reactivity of both disubstituted acetylenes means, incidentally, that the quenching by phenylacetylene can not be associated with the acetylenic proton.

The quantitative data show the acceptable range of values of x and y in equation 3 if graphs such as the one in figure 2 are to measure the rate constant for quenching by diphenylacetylene. Thus only if $k_{cd}[C_6H_5C{\equiv}CC_6H_5] > k_{cp}[C_6H_5C{\equiv}CH]$ will diphenylacetylene dominate the quenching, and this means that for $y = 1.28$, $x > 0.04$; for $y = 2.56$, $x > 0.08$; and for $y = 3.84$, $x > 0.1$. This last condition would give polypentenamers with molecular weights too small to distinguish accurately from the free poly(phenylacetylene), and accordingly the measurements of k_{cd}/k_{cc} were made for $y = 1.28$, $0 \leq x \leq 0.1$ and $y = 2.56$, $0 \leq x \leq 0.2$.

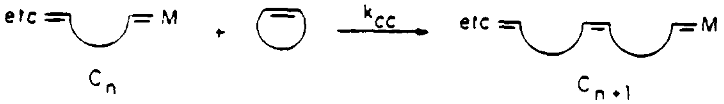
Cyclopentene as a Quencher of Poly(phenylacetylene)'s Growth. If, as we suppose in Scheme III, the quenching of poly(phenylacetylene)'s growth initiates the polymerization of cyclopentene, a similar analysis of how the size of the initiating block attached to the polypentenamer varies with the concentration of the quenching agent cyclopentene should tell what the ratio acetylene in equation 3, measures k_{cd}/k_{cc}. Since the slope of the line in figure 2 and the slope of the analogous line for experiments in which y (equation 3) was 2.56 average to 114 ± 7, it follows that for the experiments in equation 3, $k_{cd}/k_{cc} = 1.55 \pm 0.1$.

Similarly the slope, 2.84 ± 0.2, of a related graph analyzing the ability of phenylacetylene to quench the polymerization (presented above in the section on results) measures k_{cp}/k_{cc}. While the abscissa of this graph plots the amount of phenylacetylene present initially, an appreciable portion was consumed during the experiments. Accordingly the slope was multiplied by 1.52, the ratio of the amount of phenylacetylene present initially and the average of this amount and the amount remaining finally, as analyzed by the isotope dilution experiment described in the section on results. With this correction, k_{cp}/k_{cc} is estimated as 0.059 ± 0.004, implying that diphenylacetylene is 26 times as effective as phenylacetylene in quenching the metathesis reaction. The result is surprising because if the quenching involves an attack by the triple bond, the less sterically hindered monosubstituted acetylene should have been the one to react faster, but this is not so. The lower reactivity of diphenylacetylene compared to phenylacetylene is evident in its inability to initiate metatheses of cyclopentene in experiments like those above and in its measured monomer reactivity ratio at 30 °C being 1/15th that of phenylacetylene toward a poly(phenylacetylene) chain whose growth was initiated by a 1 : 1 mixture of WCl_6 and $(C_6H_5)_4Sn$ in toluene.[19] But toward the metal-carbenes studied here, diphenylacetylene was especially reactive, and it will require additional work to uncover why.

The other disubstituted acetylene briefly studied, phenylmethylacetylene, is also much more reactive than phenylacetylene in quenching the polymerization of cyclopentene. Thus the quenching by phenylmethylacetylene

Discussion

The kinetic parameters underlying the ability of phenylacetylene to initiate the metathesis of cyclopentene, and of phenylacetylene and diphenylacetylene to quench the metathesis can be determined in these experiments by analyzing how the sizes of the polymers vary as a function of the concentrations of the reagents that terminate their growth. Thus if the reactivities of the metal-carbenes, C_n, that propagate the polymerization of cyclopentene (Equation 5) do not depend on n, the number of their trailing



(5)

cyclopentene units, the rate of cyclopentene polymerization will be $v_p = k_{cc}[C_n][\text{cyclopentene}]$. If the rate constants for the quenching of these same metal-carbenes by diphenylacetylene (k_{cd}) and by phenylacetylene (k_{cp}) are also independent of n, then the number average degree of polymerization of the polypentenamer, $\bar{X}_n$, which should be the rate of polymerization divided by the rate of termination, will be given by equation 6. Accordingly, the slope of the graph in figure 2, which plots the inverse of the number average molecular weight against the amount of diphenyl-

$$\bar{X}_n = \frac{\bar{M}_n}{68.12} = \frac{k_{cc}[\text{cyclopentene}]}{k_{cd}[C_6H_5C\equiv CC_6H_5] + k_{cp}[C_6H_5C\equiv CH] + \text{other terminations}} \tag{6}$$

chains of high molecular weight and 1.5 ± 0.3% to those of low molecular weight. (In three experiments using non-radioactive phenylacetylene under the same conditions, these figures were 17.0 ± 2% and 2.4 ± 0.9% respectively.) And if all the phenylacetylene unaccounted for either by the polymer or radioactivity analyses (this is 51.8% ± 2% of the total) had been converted to free poly(phenylacetylene) that escaped collection when the polymer was precipitated (it amounts to 2 mg), the fraction of the poly(phenylacetylene) chains that initiates cyclopentene's metathesis would decrease from the *ca.* 50% estimated in the paragraph above to the minimal figure of 23 ± 3%.

Quenching by Phenylacetylene. The ability of diphenylacetylene to quench the metathesis, measured above in figure 2, can be compared with the ability of phenylacetylene to quench the same reaction. A graph similar to the one in figure 2, in which 10^6 times the inverse of the number average molecular weight of the polypentenamer formed in equation 3 when $x = 0$ is plotted against y, the equivalents of phenylacetylene used to prepare the samples, is linear. The slope of the best line through the points and through the origin is found to be 2.84 ± 0.2. An alternative way to treat the available experimental data is to graph against y the intercept in figure 2 and the corresponding intercepts when y is different. The best linear correlation (again forced through the origin) has slope 3.49 ± 0.7, not appreciably different from the first measure above. Notice that compared to diphenylacetylene, for which the analogous slope is 114, phenylacetylene is much less effective as a quencher of polypentenamer growth.

Table II here

cyclopentene. The comparison, in Table II, shows that the measurements required are difficult to make, for the yield of poly(phenylacetylene) is so small that if even one milligram were lost during the isolation (especially when y is low), the chain number listed under B in Table II would be grossly low. However not only are the true yields likely to be much higher, but the average molecular weight should probably be much lower because the material that is most likely to be lost is that with the lowest molecular weight. The error would thus be compounded. Accordingly, the UV ratio probably provides a better estimate of the fraction of poly(phenylacetylene)s that initiates polypentenamer chains, for this measure is not especially sensitive to material of low molecular weight. Assuming the molecular weights of the bound and separate poly(phenylacetylene)s to be the same (Table I and Discussion), this UV ratio is also the ratio of the chain numbers. According to this measure about 50% of the poly(phenylacetylene) chains initiate the cyclopentene metathesis reaction. However the measurements in the section below suggest that the figure may be only *ca.* half as large.

Fraction of the Phenylacetylene Consumed. The fraction of *meta*-tritiated phenylacetylene remaining after reaction according to equation 3 when x = 0.0 and y = 1.28 was measured by diluting the quenched reaction mixture with non-radioactive phenylacetylene and analyzing the radioactivity of a sample recovered by precipitating the silver salt and converting it back to the hydrocarbon. The experiment (repeated twice) showed that 31.2 ± 1% of the phenylacetylene remained. Of the 69.8% consumed, 15.4 ± 2% was gauged by UV analysis of the gel permeation chromatograms to be attached to the polymer (as measured by experiments like those in figure 2, see Table III below) is only 42 % that of diphenylacetylene.

Second, the size of the initiating block, which can be seen in figure 7 to consist of 14 - 31 phenylacetylene units (the molecular weight of phenylacetylene is 102), rises with the amount of phenylacetylene used for the experiments. Figure 8 displays the inverse of the molecular weights of these initiating blocks, measured in figure 7 and averaged with additional measurements (see Table I), as a function of the inverse of the equivalents of phenylacetylene in the reaction mixtures. The best straight line (least squares) that accommodates the points and that goes through the origin is displayed, as is the slope.

Third, the molecular weight of the initiating block of poly(phenylacetylene) can be compared with the molecular weight of the poly(phenylacetylene) that does not initiate polypentenamer chains, and which presumably gives rise to the peak at low molecular weight in the gel permeation chromatograms (Figure 4). The comparison is summarized in Table I. As elaborated in the Discussion Section, the molecular weights of the unattached (also called below "free") and attached polyacetylene units are seen to be similar.

Table I here

Fraction of the Poly(phenylacetylene)s That Initiates Polypentenamer Chains. Related to this last point is a comparison of the number of polypentenamer and free poly(phenylacetylene) chains, for this tells what fraction of the poly(phenylacetylene)s initiates the polymerization of of the weight of polypentenamer and the weight of poly(phenylacetylene) attached to the polypentenamer, and (2) the number average molecular weight of the polypentenamer. The data are for four series of experiments in which the amount of phenylacetylene (y in equation 3) was held constant at 1.28, 2.56, or 3.84 equivalents (as labeled in figure 7 in parentheses at the upper left of each graph) and the amount of diphenylacetylene or, in one experiment, phenylmethylacetylene was varied. Equation 4 shows that the functional relationship between the ratio and the molecular weight should be linear if the size of the initiating block does not depend on the concentration of diphenylacetylene. The slope should then be the inverse of the number average molecular weight ($\bar{M}_{np}$) of the poly(phenylacetylene)

$$\frac{\text{weight of polypentenamer}}{\text{weight of poly(phenylacetylene)}} = \frac{N_c\bar{M}_{nc}}{N_c\bar{M}_{np}} = \left(\frac{1}{\bar{M}_{np}}\right)\bar{M}_{nc} \qquad (4)$$

attached to the polypentenamer chains (whose number average molecular weights are $\bar{M}_{nc}$). Since the ratio of the two weights is simply the ratio of the areas under the RI and UV peaks at high molecular weight in the gel permeation chromatograms multiplied by a measurable calibration constant, and the procedure allows for the point (0,0) to be on the line, this is the method we used to measure the size of the initiating poly(phenylacetylene) unit.

Three points about the data in figure 7 are noteworthy. One is that the size of the initiating block is measured to be the same whether the quenching agent is diphenylacetylene (Figure 7b) or phenylmethylacetylene (Figure 7a), which is reasonable since the quenching can not alter the initiating block. The effect is probably not coincidental, for the ability of the phenylmethylacetylene to quench the growth of polypentenamer chains measure the mass of the polypentenamer flowing from the chromatograph, while the ultraviolet monitor should measure the number of chains. If it is assumed that the RI and UV intensities both measure polymer mass, the number average molecular weights according to the RI analysis are (for a series of four experiments in which y in equation 3 was 1.28) 2.34 ± 0.2 times those according to the UV analysis.[17] But if the RI intensities measure mass, while the UV intensities measure chain number, the discrepancy (which is in the opposite direction) is, as it should be, smaller: the number average molecular weights according to the UV analysis are 1.28 ± 0.11 times as large as those according to the RI. According to the theory, the UV peak should be shifted even further to the right of the RI peak, corresponding in the Kennedy analysis (Figure 6) to the observed deviation from the line of the point at highest mass. The Kennedy analysis has been applied previously only to polymers one tenth as large, and the observed deviation may be caused by small errors in the measurements of molecular weights that are high. (Elution times are then particularly insensitive to small changes in mass.) Whatever the origin of the deviation, however, the essential point that the UV peaks are always to the right of the RI peaks seemingly can not be accounted for other than by presuming that the UV absorbing species are present at the initiating end of the polypentenamer.

The Size of the Initiating Block. The size of the initiating block can be measured by dividing the total weight, displayed in figure 5, of poly(phenylacetylene) attached to polypentenamer chains by the number of polypentenamer chains per sample, displayed in figures 3 and 9. But the following procedure, which measured sizes somewhat higher (ca. 13 %), is probably more accurate. Figure 7 displays the data required: (1) the ratio

10 min in a 27 °C water bath, the reactions were doused with *ca*. 2 mL CH_3OH saturated with NH_3. The products were transferred with additional CH_3OH-NH_3 to 20 mL centrifuge tubes and after centrifuging, isolating the precipitates, and washing further with CH_3OH-NH_3 and pure CH_3OH, the polymeric products were pumped dry at 0.2 torr until their weights were constant to < 0.7 mg.

Analyses. The gel permeation chromatographic analyses were performed using five serially connected μ-styragel columns from Waters Associates (10^6, 10^5, 10^4, 10^3, and 500 Å) and THF pumped at ambient temperature at 2.0 mL/min by a Waters M6000A pump. The RI monitor was Waters' Model R401, and the UV monitor Schoeffel Instruments' Model SF 770. The UV detector was fixed at 254 nm because the absorption spectrum of poly(phenylacetylene) has an intense shoulder at this wavelength,[3] because samples of poly(phenylacetylene) with different molecular weights (prepared in C_6H_5Cl with different amounts of WCl_6: 1/22.2 equivalents, "$\bar{M}_n$" $= 2.9 \times 10^3$; 1/4.3 equivalent, "$\bar{M}_n$" $= 1.3 \times 10^3$) showed similar extinction coefficients (32 and 38 L/g cm), and because polypentenamer absorbs negligibly at this wavelength. This last point was established using a sample prepared from cyclopentene, WCl_6, and $C_6H_5C{\equiv}CH$ (200 : 1 : 2) in C_6H_5Cl at 28 °C (11 min), which had an absorption per gram that was < 0.8 % as intense as that of poly(phenylacetylene) and using a sample prepared in 1.5 % yield from cyclopentene with WCl_6 (200 : 1, no phenylacetylene) in C_6H_5Cl at 31 °C for 21 h,[32] which absorbed even less per gram [< 0.07% that of poly(phenylacetylene)]. The ^1H NMR spectrum showed this last polymer to be largely polypentenamer (93 % according to measurements on the allylic and non-allylic saturated protons, 85 % according to measurements on the olefinic and non-olefinic protons).

Samples of the polymers (ca. 7 - 9 mg) were dissolved in 10 mL THF (stirring overnight), filtered through celite and then through a 0.5 m filter (there was no obvious gel), and 0.30 mL portions were inserted into the chromatograph's injector. The analyses were performed two days after the preparation of the polymers began, and molecular weights were calibrated using seven polystyrene standards ($\bar{M}_n \times 10^{-3}$ = 929, 392, 254, 111, 20.4, 8.5, and 3.3) every time measurements were made. The molecular weights associated with the low-mass [poly(phenylacetylene)] peaks, recorded as the molecular weights of the polystyrenes that would have the chromatograms observed, are presented in quotation marks. The quotation marks are removed when these masses are divided by 1.5.[18] The molecular weights recorded for the high-mass (polypentenamer) peaks (not in quotation marks) are those according to the polystyrene standards divided by two.[10]

Overlapping peaks were analyzed by drawing on strip-chart recordings plausible chromatograms that sum to the chromatograms observed. The response of the RI detector was calibrated using two samples of polypentenamer prepared from cyclopentene, WCl_6, $C_6H_5C{\equiv}CH$, and $C_6H_5{\equiv}CCH_3$ (200 : 1 : 1.28 : 0.1 or 0.2) in 0.5 mL C_6H_5Cl at 27 °C for 11.5 min. The areas under the RI peaks were $(1.303 \pm 0.04) \times 10^4$ units/mg. Similarly, using a sample of poly(phenylacetylene) prepared from $C_6H_5C{\equiv}CH$ and WCl_6 (200 : 1, in C_6H_5Cl, 20 °C, 5 min, "$\bar{M}_n$" = 1.4×10^4), the area under the 254 nm absorption peak was measured as $(8.939 \pm 0.08) \times 10^5$.

The assumption that the ratios of the concentrations of cyclopentene and phenylacetylene remain constant throughout the experiments would be justified if the extents of reaction were small. Estimates of how much this ratio changes during the course of the experiments, average 20 ± 12 %, but this means that the average ratio differs from the initial ratio by only ca. 10 %. The problems associated with possible losses of small amounts of low molecular weight poly(phenylacetylene) plague these measurements as they do those discussed in connection with Tables I and II. The analytical data and yields for 37 experiments are summarized in a series of experimental tables in the supplementary material.

Fraction of Unconsumed Phenylacetylene. Meta-tritiated phenylacetylene was prepared from 1-(m-bromophenyl)-2-trimethylsilylacetylene (10.4 g) and 50 mCi (0.5 mL) T_2O, essentially according to a procedure used to make the m-deuterio analogue.[33,34] The protecting trimethylsilyl group was removed with the aid of 80 mL 0.1 M $(\underline{m} - C_4H_9)_4NF$ in tetrahydrofuran at room temperature.[36] Extraction and distillation through a spinning band column gave 3.0 g (71.5% yield) of phenylacetylene (analyzed by ^{1}HNMR), which after dilution with 10 g common phenylacetylene (96.1% pure, 3.9% styrene, vpc analysis) and redistillation (spinning band) gave material that according to vpc analysis was 97.6% phenylacetylene and 2.4% styrene. Samples of known concentration (UV analysis) in 2 mL hexane when analyzed by liquid scintillation counting in 10 mL of Beckman's Ready-solv™ NA cocktail[37] recorded (498 ± 6.9) x 10^3 cpm/0.216 mg of sample.

A mixture of 4 μL (3.7 mg) of this acetylene and cyclopentene (0.5 mL) was combined as above with 0.5 mL of a solution of 227.4 mg WCl_6 in 10 mL C_6H_5Cl. After 10 min at 27 °C and dousing as before, the mixture was shaken with 1.000 g non-radioactive phenylacetylene. The polymer was then centrifuged, isolated, and analyzed as previously, while the supernatant was treated in portions with a total of 7.4 g $AgNO_3$ in a mixture of 20 mL CH_3OH, 30 mL H_2O, and *ca.* 5 mL conc. NH_4OH. The precipitated silver salt was decomposed by 10 g NaCN in *ca.* 50 mL H_2O, and after extraction (ether), washing, drying, and kukelrohr distillation, gave 1.025 g of phenylacetylene in ether (65.8% phenylacetylene according to vpc analysis, a 67% recovery). The concentration of a solution in *n*-hexane was analyzed by UV spectroscopy, and 2 mL samples in 10 mL cocktail when analyzed by liquid scintillation counting recorded $(7.32 \pm 0.17) \times 10^3$ cpm/2.656 mg.[38] This means that 32.3% of the phenylacetylene remains. In a repetition of the experiment[39] the fraction of residual phenylacetylene was similarly measured as 30.2%.

The polymer analyses showed that in the two experiments the yields of polypentenamer were 25.6 and 27.2%, the fraction of the initially present phenylacetylene that was attached to the polypentenamer as poly(phenylacetylene) was 13.1 and 17.8%, while the yield of "free" poly(phenylacetylene) was 1.2 and 1.8%. These figures are comparable to those for similar samples described in the supplemental material, as well as for two others: yield of polypentenamer 29.0%, 19.8%; yield of attached poly(phenylacetylene) 14.2,-%; yield of free poly(phenylacetylene) 1.8,-%.

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Supplementary Material Available: Analytical data and yields for 37 experiments (10 pages). Ordering information is given on any current masthead page.

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(38) The analysis of unlabelled phenylacetylene (the "background") was 21 cpm and the counting efficiency measured by the instrument for all samples was the same.

(39) In this experiment, the polymer was separated before the 1.000 g of phenylacetylene was added to the reaction product.

Figure Captions

Figure 1. The yield in milligrams and % of polypentenamer formed from 387 mg cyclopentene in equation 3 ($y = 2.56$) as a function of the amount of diphenylacetylene in milligrams and equivalents (x in equation 3). The yield of polypentenamer is the total weight of polymer precipitated by methanol less the miniscule (and negligible) total content of poly(phenylacetylene) analyzed by UV spectroscopy.

Figure 2. The inverse (times 10^6) of the number average molecular weight of polypentenamer formed in equation 3 when $y = 1.28$ equivalents as a function of the amount of diphenylacetylene (x) used. The results of two sets of experiments are combined, in one of which the reaction time was a minute longer. The molecular weights of the polypentenamers were derived by analyzing the peaks at high molecular weight in the gel permeation chromatograms (see figure 4). The minute contributions of poly(phenylacetylene) to these peaks were ignored. The straight line that, by the method of least squares, best fits the points is displayed. Its slope is 117 ± 11.

Figure 3. The total weight of the polymer samples obtained after precipitation with methanol and drying as a function of the number average molecular weight of the polypentenamer each contains. The reaction mixtures are described in equation 3, the amount y of phenylacetylene (displayed in the lower right corners) being constant in each of the four series of experiments, while x, the amount of diphenylacetylene, varied. The reaction

time was 11 min for graph a and 10 min for the others. The molecular weights of the polypentenamers were derived by analyzing the peaks at high molecular weight in the gel permeation chromatograms (see figure 4). Displayed are the best straight lines according to the method of least squares and their slopes (N_c).

Figure 4. Gel permeation chromatograms of three polymer samples prepared according to equation 3, with y = 1.28 and x = 0.00, 0.03, and 0.08. Five μ-styragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å) from Waters Associates were used at ambient temperature, and tetrahydrofuran flowing at 2 mL/min was the solvent. The chromatograms were monitored simultaneously using a RI monitor (curves marked "RI") and a UV monitor that measured absorption at 254 nm (curves marked "UV"). The weights of the samples analyzed in these three chromatograms were 0.23 mg when x = 0, 0.19 mg when x = 0.03, and 0.27 mg when x = 0.08. The vertical line through the center of the third curve is drawn to clarify the relative positions of the peaks.

Figure 5. For samples of polymer prepared according to equation 3 with y = 1.28, 2.56, and 3.84, the total UV absorption intensity per sample under the peak at high molecular weight [converted to mg of poly(phenylacetylene), called PPA, using the measured absorption intensity per mg] is displayed as a function of x, the number of equivalents of diphenylacetylene.

Figure 6. An analysis after Kennedy (reference 15) of a gel permeation chromatogram, like the ones in figure 4, with x = 0.06. The ratio of the intensity recorded by the UV and RI monitors at the RI peak maximum (labelled with an m) divided by this ratio at variable elution times, x, as

a function of the ratio of the molecular weights of polypentenamer eluted at times x and at the peak maximum.

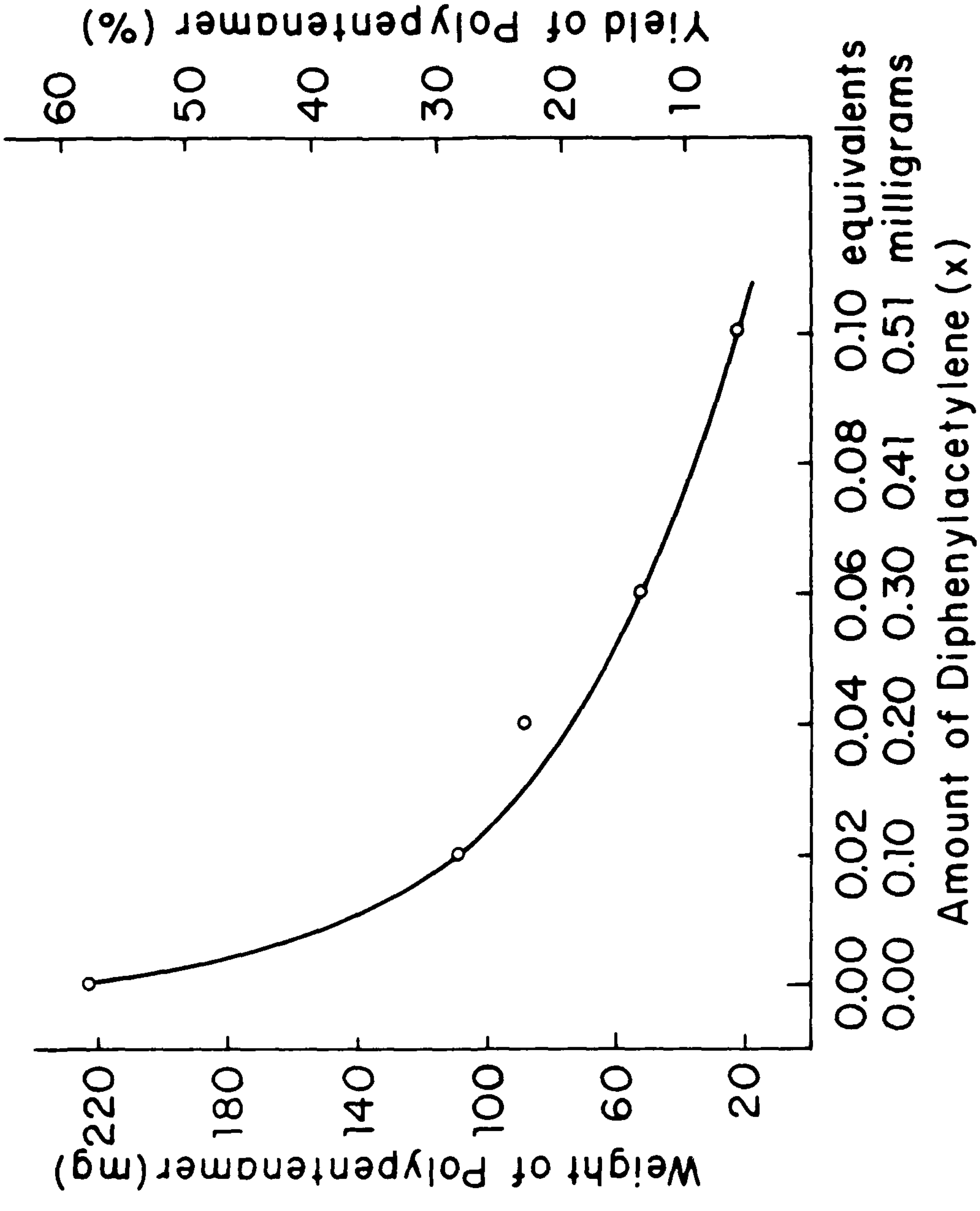
Figure 7. Determination of the number average molecular weights of the poly(phenylacetylene) blocks initiating the polypentenamer chains. The samples for each series of experiments were made according to equation 3 (the reaction times varied slightly), with fixed amounts of phenylacetylene, recorded in parentheses in the upper left corners of each graph, and varying amounts of disubstituted acetylene, $C_6H_5C{\equiv}CR$, where R = C_6H_5 or CH_3. The weight of polypentenamer divided by the weight of poly(phenylacetylene) attached to the high molecular weight chain is plotted as a function of the number average molecular weight of the polypentenamer. The molecular weights of the polypentenamers were measured as for figure 3. The reaction times during which the samples were prepared were 11.5 min for those in graph a, 11 min for those in b, and 10 min for the others.

Figure 8. The inverse of the number average molecular weight of the initiating poly(phenylacetylene) block attached to the polypentenamers as measured in figure 7 and averaged with additional data (see Table I) as a function of the inverse of the number of equivalents of phenylacetylene used in the preparation of the polymers. The least squares line through the origin that best fits the points is displayed.

Figure 9. The number of polypentenamer chains (N_c, formed in equation 3) as a function of the amount of phenylacetylene (y). The chain numbers are those displayed in figure 3b and c, the average of the number in figure 3d and the number [$(1.192 \pm 0.08) \times 10^{-6}$] measured when the experiment in

figure 3d was repeated, and zero, the expected chain number when there is no phenylacetylene. The best straight line by the method of least squares that goes through the origin is displayed. Its slope is 0.313 ± 0.02.

Figure 1


Weight of Polypentenamer (mg)
220
180
140
100
60
20
Yield of Polypentenamer (%)
60
50
40
30
20
10
0.00 0.02 0.04 0.06 0.08 0.10 equivalents
0.00 0.10 0.20 0.30 0.41 0.51 milligrams
Amount of Diphenylacetylene (x)

S-2. $y = 2.56$

henylacetylene [a]	0.00	0.02	0.04	0.06	0.10	0.20
a High MW [b-1]	1979.7±103.4	2832.9±192.3	2695.6±285.7	3186.5±509.9	5152.5±163.0	5415. ±45.70
a Low MW [b-2]	259.9± 6.4	989.4± 33.2	913.7±102.2	1809.9±208.8	3139.4±276.7	2880.8± 4.7
jected (mg) [b-3]	0.00251	0.00427	0.00404	0.00559	0.00928	0.00928
(mg/mL) [c-1]	0.76	0.82	0.60	0.61	0.79	0.75
ion Volume (mL) [c-2]	0.3	0.3	0.3	0.3	0.3	0.3
r Injected (mg) [c-3]	0.228	0.246	0.180	0.183	0.237	0.225
g/mg polymer) [c-4]	0.0113	0.0174	0.0224	0.0305	0.0392	0.0412
r yield (mg) [d-1]	225.55	111.45	91.15	53.95	23.75	5.65
eld (mg) [d-2]	2.48	1.94	2.04	1.65	0.93	0.23
(%) PPA total [d-3]	33.3	26.0	27.4	22.1	12.5	3.1
VLA [e-1]	7.64±0.59	2.87±0.10	2.95±0.02	1.75±0.08	1.65±0.09	1.88±0.16
n High MW (mg) [e-2]	2.19	1.44	1.52	1.05	0.58	0.15
n Low MW (mg) [e-3]	0.29	0.50	0.52	0.60	0.35	0.08
entenamer (mg) [f-1]	223.07	109.51	89.11	52.30	22.82	5.42
$\bar{M}_n$ (High MW) [f-2]	153.1±7.1	109.8±3.2	95.9±7.5	71.1±3.5	53.9±1.3	35.1±4.[illegible]
$_c$ (mole) [f-3]	1.47	1.01	0.95	0.75	0.43	0.16
$\bar{M}_w$ (Low MW) [g-1]	10.74±0.31	6.13±0.10	5.80±0.19	7.64±0.41	7.57±0.45	7.25±0.[illegible]
$\bar{M}_n$ (Low MW) [g-2]	4.52±0.01	2.07±0.11	2.10±0.00	2.63±0.03	2.85±0.23	2.89±0.[illegible]
$_p$ (mole) [g-3]	0.06	0.24	0.26	0.23	0.12	0.03
$\bar{M}_n$ PPA on High MW [h]	1.44	1.43	1.60	1.40	1.35	0.94
(%) Polypentenamer [i]	57.6	28.3	23.[illegible]	13.5	5.9	1.4
ea High MW (x 1) [j-1]	[illegible]	[illegible]±87.1	1411.2±351.8	1905.1±235.6	2390.9±55.6	1723.[illegible]
olypentenamer/wt. PPA High [j-2]	40.2	60.7	47.9	41.1	31.8	21.3
$\bar{M}_w$ High [k]	304.5±11.2	237.1±11.3	167.4±7.2	134.4±8.2	87.7±3.6	60.3±4.[illegible]
Change in C≡C/C=C [ℓ]	+28.[illegible]	+1.6	-2.8	-4.9	-3.5	-0.8

S-1. y = 1.28

phenylacetylene [a]	0.00	0.02	0.04	0.06	0.10
a High MW [b-1]	1279.3 ± 29.2	3047.2 ± 121.1	3732.3 ± 7.0	4718.8 ± 26.0	6064.0 ± 14.7
a Low MW [b-2]	130.6 ± 16.7	618.7 ± 95.3	960.5 ± 41.2	1172.7 ± 115.1	1688.1 ± 94.0
jected (mg) [b-3]	0.00158	0.00410	0.00525	0.00659	0.00867
(mg/mL) [c-1]	0.79	0.82	0.84	0.83	0.82
ion Volume (mL) [c-2]	0.30	0.30	0.30	0.30	0.30
r Injected (mg) [c-3]	0.237	0.246	0.252	0.249	0.246
ng/mg polymer) [c-4]	0.00667	0.01667	0.02083	0.02647	0.03524
er yield (mg) [d-1]	117.05	52.10	43.80	27.55	19.00
ield (mg) [d-2]	0.78	0.87	0.91	0.73	0.67
(%) PPA total [d-3]	20.9	23.3	24.4	19.6	18.0
UVLA [e-1]	9.99 ± 1.50	5.02 ± 0.58	3.89 ± 0.16	4.06 ± 0.38	3.60 ± 0.19
n High MW (mg) [e-2]	0.71	0.73	0.72	0.59	0.52
n Low MW (mg) [e-3]	0.07	0.14	0.19	0.14	0.15
entenamer (mg) [f-1]	116.27	51.23	42.89	26.82	18.33
$\bar{M}_n$ (High MW) [f-2]	188.6 ± 6.3	94.4 ± 2.1	90.2 ± 5.4	75.2 ± 8.1	57.8 ± 4.1
$_c$ (mole) [f-3]	0.620	0.550	0.480	0.360	0.330
$\bar{M}_w$ (Low MW) [g-1]	10.39 ± 0.51	10.38 ± 0.76	10.21 ± 1.02	11.13 ± 1.23	10.52 ± 1.96
$\bar{M}_n$ (Low MW) [g-2]	4.73 ± 1.03	5.44 ± 0.49	4.73 ± 0.41	5.15 ± 0.42	5.21 ± 0.73
$_p$ (mole) [g-3]	0.015	0.026	0.041	0.027	0.029
$\bar{M}_n$ PPA on High MW [h]	1.15	1.33	1.50	1.64	1.58
(%) Polypentenamer [i]	30.0	13.2	11.1	6.9	4.7
ea High MW (x 1) [j-1]	3239.9 ± 131.4	3143.0 ± 97.5	3398.3 ± 28.4	3362.7 ± 119.3	3339.5 ± 75.2
olypentenamer/wt. PPA High [j-2]	172.4	70.4	62.5	48.8	37.7
$\bar{M}_w$ High [k]	438.6 ± 32.9	200.0 ± 19.2	178.5 ± 18.2	156.8 ± 22.0	112.5 ± 13.9
Change in C≡C/C=C [l]	+6.5	-5.8	-7.5	-6.8	-7.0

Supplementary Material

A Procedure Identifying a Polyacetylene Initiator of Olefin Metathesis. The Reactivities of Metal-Carbenes Toward Alkenes and Alkynes

Chien-Chung Han and Thomas J. Katz*

The Tables below summarize the yields and gel permeation chromatographic analyses of the polymers formed according to equation 3, with differing amounts of phenylacetylene (y equivalents) and diphenylacetylene (x equivalents). In each experiment 387 mg cyclopentene (5.68 mmol, 200 equivalents) was combined in 0.5 mL C_6H_5Cl with 11.3 mg WCl_6 (0.0285 mmol, 1 equivalent), 2.90 y mg phenylacetylene (0.0284 y mmol, y equivalents), and 5.06 x mg diphenylacetylene (0.0284 x mmol, x equivalents). For the experiments in Table S-6 phenylmethylacetylene was substituted for diphenylacetylene. Reactions were carried out at 27 °C for 10 min for the experiments in Tables S-1 - S-4, for 11 min for those in Table S-5, and 11.5 min for those in Table S-6. The footnote numbers when enclosed in parentheses designate the values of the data to which they refer.

Table III. Ratios of Rate Constants for the Reactions (Equation 3) of Metal-Carbenes C_n (Equation 5) with $C_6H_5C{\equiv}CR$ (R = C_6H_5, CH_3, H) and with Cyclopentene and k_{pp}/k_{pc} as Defined in Scheme III and Equation 7

	R			
	C_6H_5	CH_3 [a]	H (Eq 3) [b]	H (Eq 1) [b]
k_{cx}/k_{cc} [c]	1.55 ± 0.1	0.646 ± 0.04	0.059 ± 0.004	0.046 ± 0.001
k_{pp}/k_{pc}			$(2.9 \pm 0.4) \times 10^3$	$(2.8 \pm 0.2) \times 10^3$

[a] The reactions were carried out as in equation 3, but with phenylmethylacetylene (0.0 - 1.0 equivalents) in place of diphenylacetylene. The reaction time was 11.5 min. [b] Reaction 1 was effected in a vacuum with no solvent (see reference 5c). Reaction 3 was effected in chlorobenzene (as shown) and in the atmosphere. These rate ratios have been multiplied by 1.52 to correct (see text) for phenylacetylene consumed. The factor was measured only for experiments according to eq 3, but may be approximately valid for those according to eq 1 because the measured yields of polypentenamer and poly(phenylacetylene) were similar in the two experiments. [c] k_{cx} is k_{cd} when R = C_6H_5, k_{cm} when R = CH_3 and k_{cp} when R = H.

Table II. The Number of Chains of Polypentenamer and of Free Poly(phenylcetylene) Formed in Equation 3, the Yield of Poly(phenylacetylene), and the Ratio of Integrated UV Intensities Under the High and Low Molecular Weight Gel Permeation Chromatographic Peaks

y in Eq 3	Number of Chains x 10^6 (mol): Polypentenamer (A)[a]	Poly(phenylacetylene) (B)[b]	A/B	Yield (mg) of poly(phenylacetylene)[c]	UV Ratio[d]
1.28	0.480 ± 0.03	0.027 ± 0.009	18	0.14	4.14 ± 0.4
2.56	0.906 ± 0.05	0.180 ± 0.09	5.0	0.45	2.22 ± 0.6
3.84	1.105 ± 0.09	0.638 ± 0.12	1.7	1.70	1.58 ± 0.2

[a] See figure 9. [b] The yield of poly(phenylacetylene) divided by its number average molecular weight (Table I). [c] The weight of the total polymer x the ratio of the UV absorption per mg under the low molecular weight gel permeation chromatographic peak and the absorption per mg for pure poly(phenylacetylene). The weights of phenylacetylene in the reaction mixtures were 3.73, 7.45, and 11.15 mg. [d] The ratio of the areas under the gpc peaks at high and low mass.

Table I. Comparison of the Molecular Weights of the Poly(phenylacetylene) Attached to Polypentenamer Chains and Not So Attached

	$10^{-3} \times \bar{M}_n$			
		Unattached		
y in Eq. 3	Attached [a]	Raw Data [b,c]	Corrected [d]	Ratio [e]
1.28	1.42 ± 0.01	5.98 ± 1.1	4.0	0.36
2.56	1.77 ± 0.05	3.76 ± 0.5	2.5	0.71
3.84	2.87 ± 0.08	4.72 ± 0.5	3.1	0.93

[a] Determined as in figure 7 and averaged with additional such experiments in which y was 1.28 and 3.84. [b] Molecular weights according to gel permeation chromatographic analysis, recorded as those of polystyrenes that would exhibit the chromatograms observed. [c] The molecular weights do not vary systematically with x in equation 3, and are averaged both for a variety of x values, for repeated measurements, and for repeated preparations of the samples. [d] The raw data is divided by 1.5 to take account of the reported differences between the chromatograms of polystyrene and poly(phenylacetylene)---see reference 18. [e] The ratio of the data under the columns labeled "Attached" and "Corrected."

Figure 9

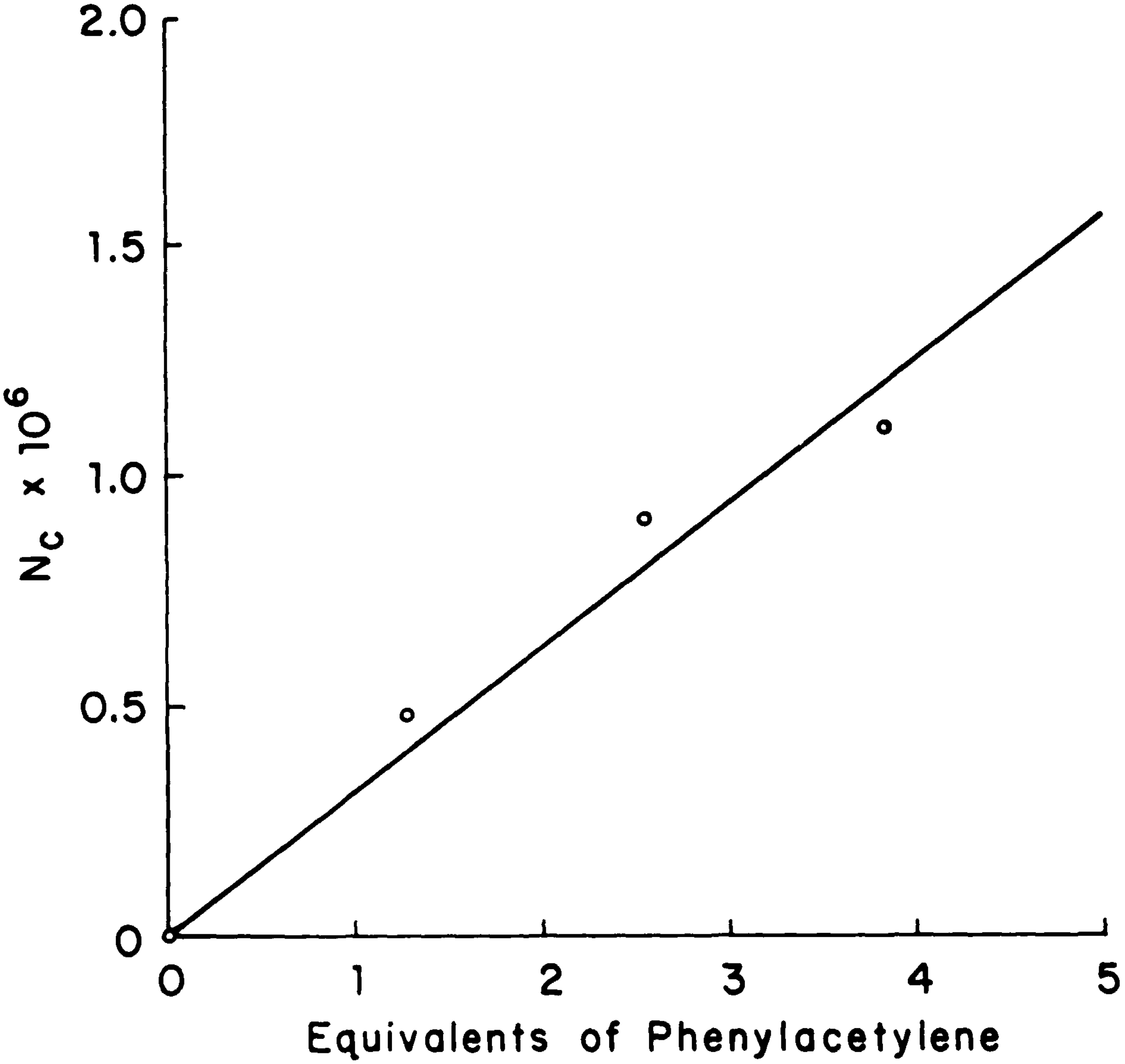
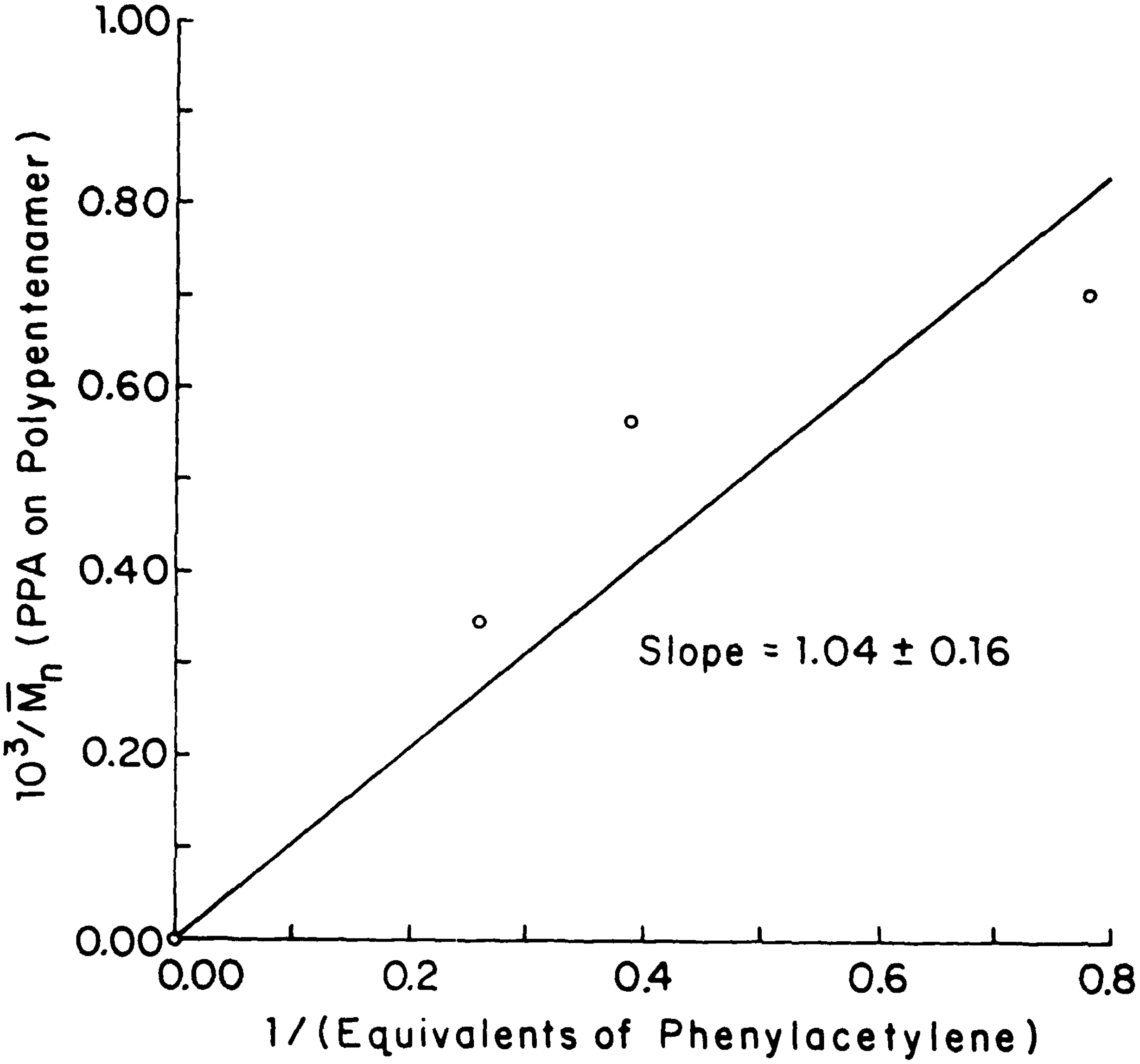

2.0
1.5
1.0
0.5
0
$N_c \times 10^6$
0
1
2
3
4
5
Equivalents of Phenylacetylene

Figure 8



1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.2
0.4
0.6
0.8
$10^3/\bar{M}_n$ (PPA on Polypentenamer)
1/(Equivalents of Phenylacetylene)
Slope = 1.04 ± 0.16

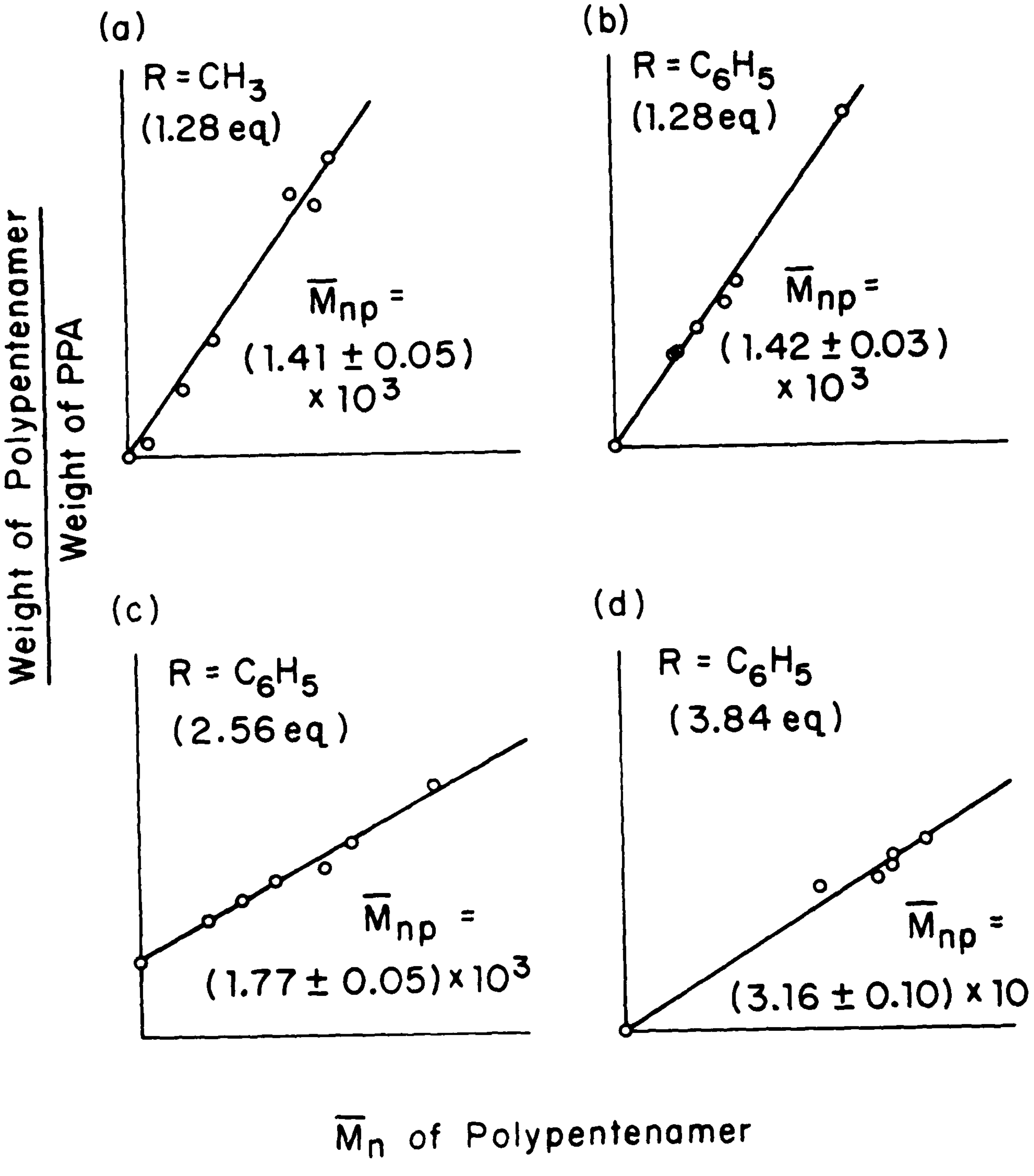
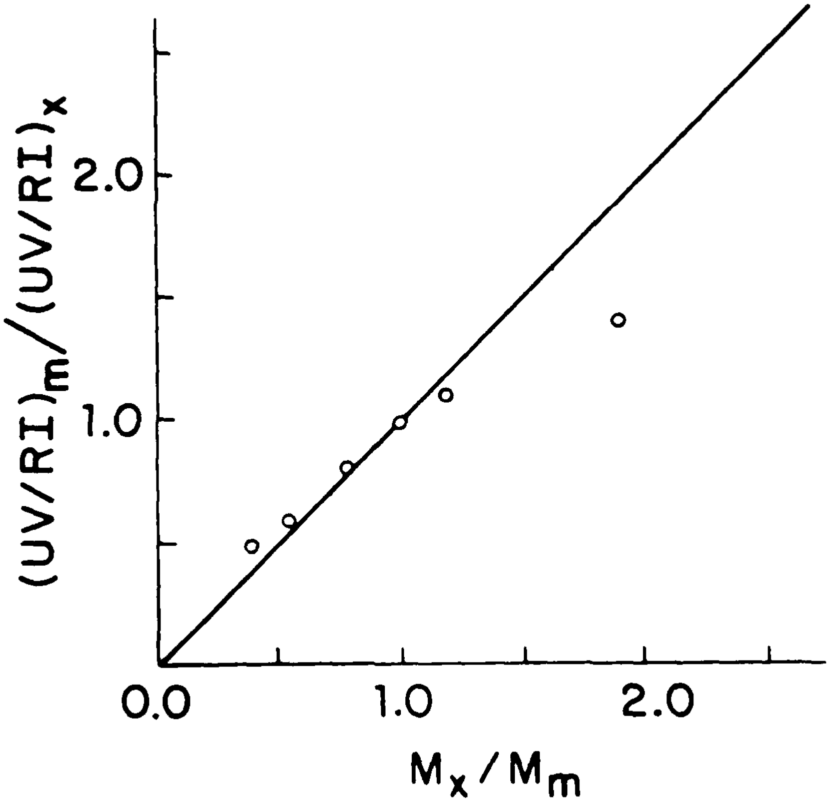

(a)
R = CH_3
(1.28 eq)
$\overline{M}_{np}$ = (1.41 ± 0.05) x 10^3
(b)
R = C_6H_5
(1.28 eq)
$\overline{M}_{np}$ = (1.42 ± 0.03) x 10^3
(c)
R = C_6H_5
(2.56 eq)
$\overline{M}_{np}$ = (1.77 ± 0.05) x 10^3
(d)
R = C_6H_5
(3.84 eq)
$\overline{M}_{np}$ = (3.16 ± 0.10) x 10^3
Weight of Polypentenamer / Weight of PPA
$\overline{M}_n$ of Polypentenamer

Figure 6



A-C 7791 WL

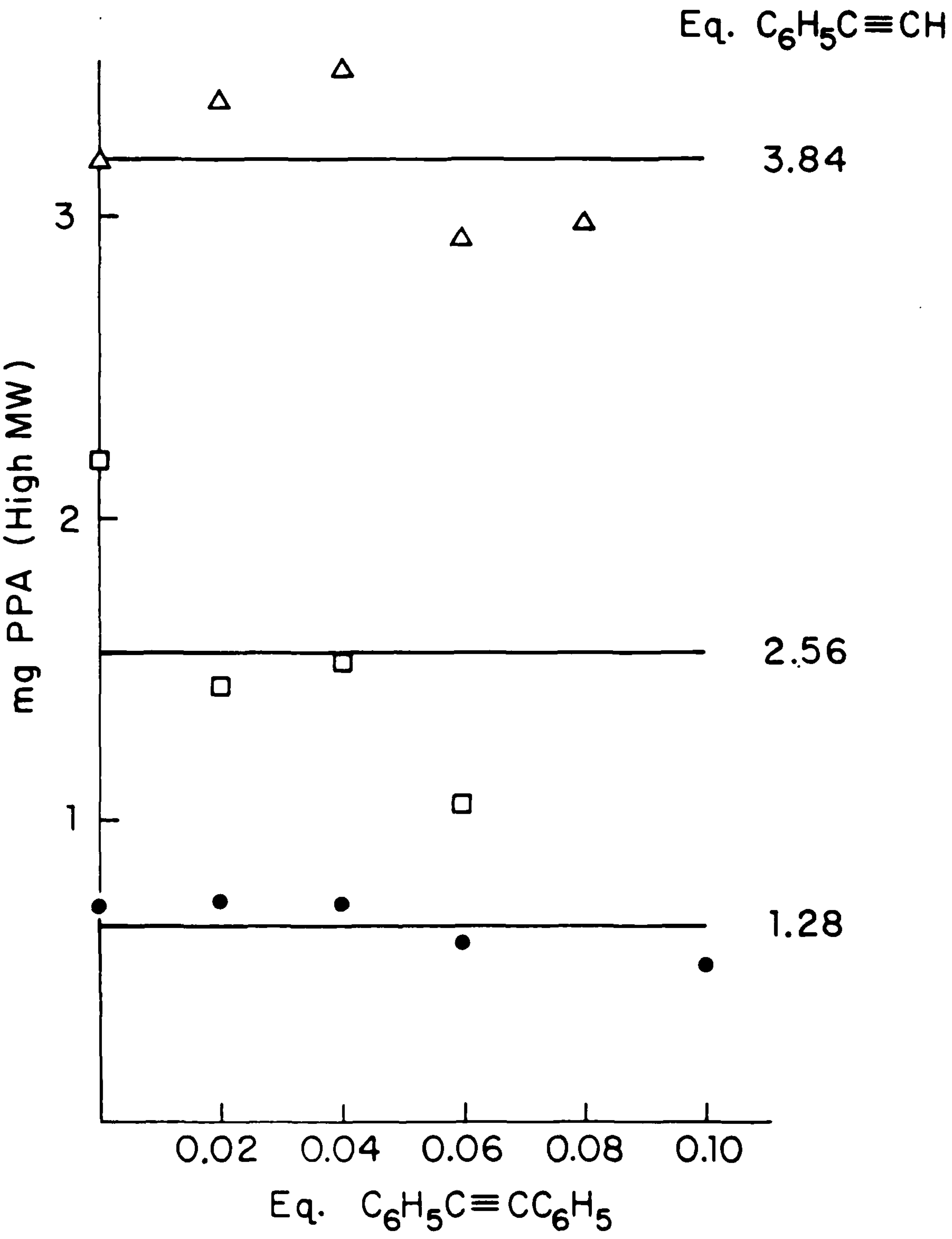

Eq. $C_6H_5C{\equiv}CH$
3.84
2.56
1.28
mg PPA (High MW)
1
2
3
0.02
0.04
0.06
0.08
0.10
Eq. $C_6H_5C{\equiv}CC_6H_5$

Figure 4

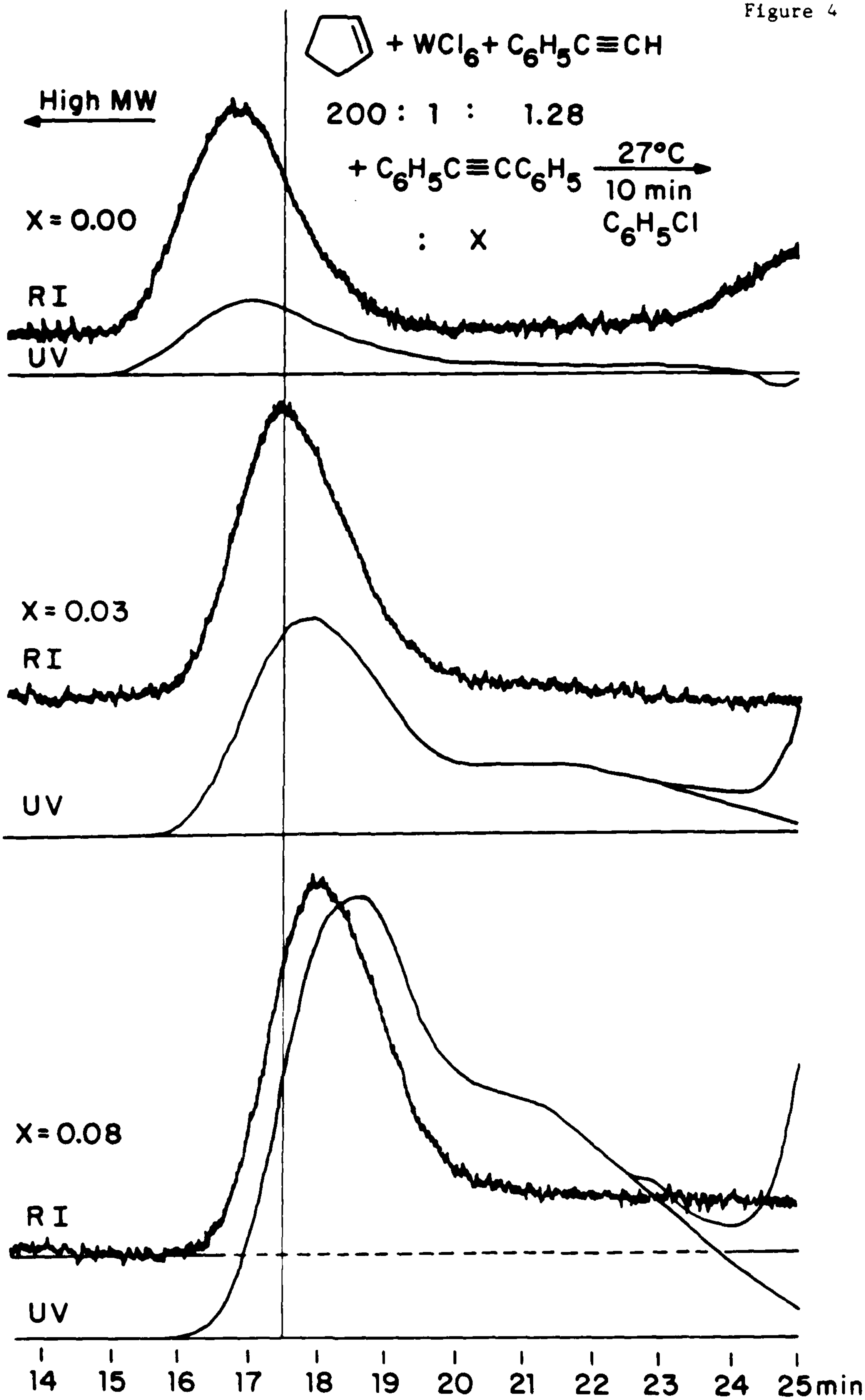

+ WCl6 + C6H5C≡CH
200 : 1 : 1.28
+ C6H5C≡CC6H5
: X
27°C
10 min
C6H5Cl
High MW
X = 0.00
RI
UV
X = 0.03
RI
UV
X = 0.08
RI
UV
14
15
16
17
18
19
20
21
22
23
24
25 min

Figure 3

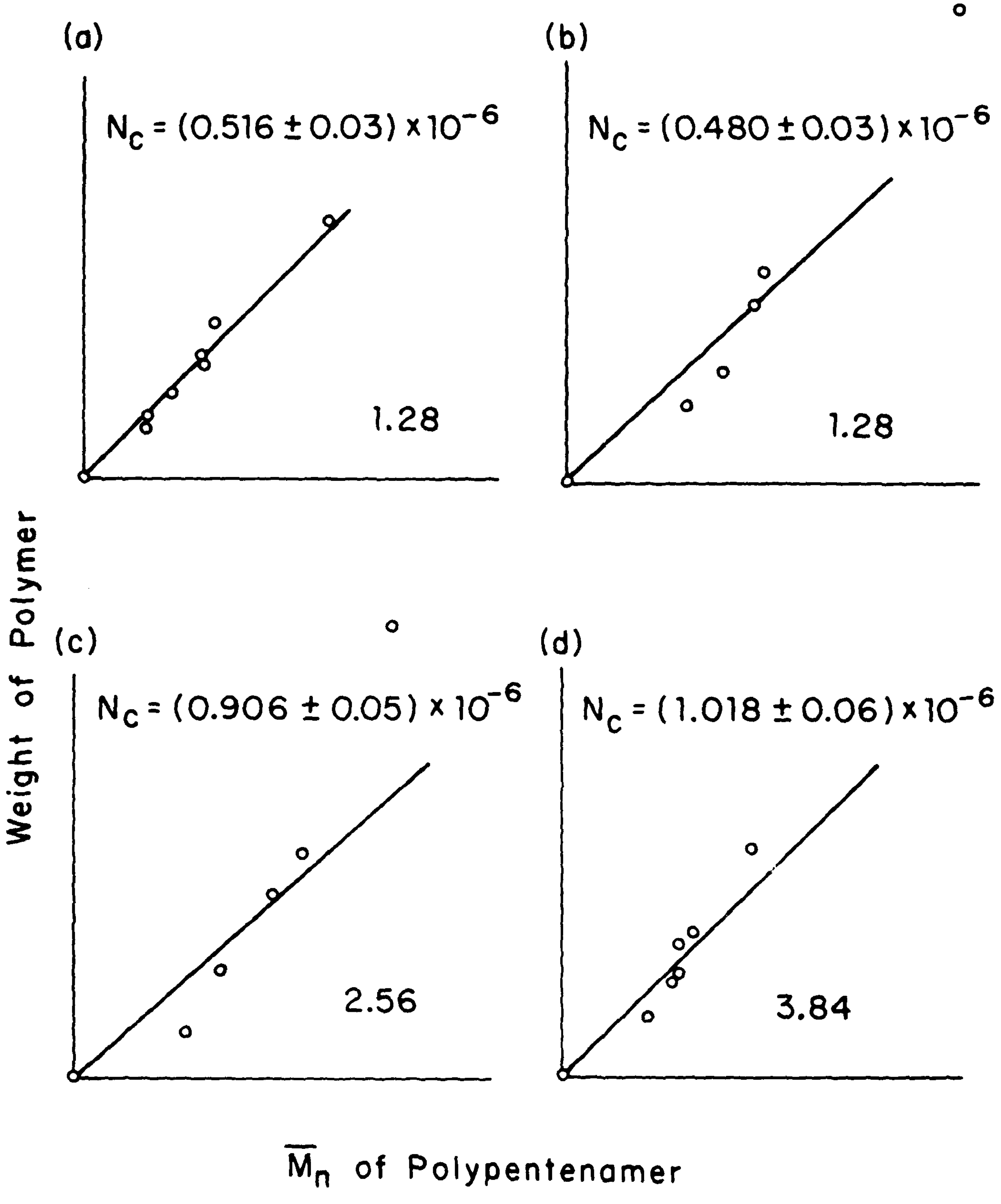

(a)
$N_c = (0.516 \pm 0.03) \times 10^{-6}$
1.28
(b)
$N_c = (0.480 \pm 0.03) \times 10^{-6}$
1.28
(c)
$N_c = (0.906 \pm 0.05) \times 10^{-6}$
2.56
(d)
$N_c = (1.018 \pm 0.06) \times 10^{-6}$
3.84
Weight of Polymer
$\overline{M}_n$ of Polypentenamer

Figure 2

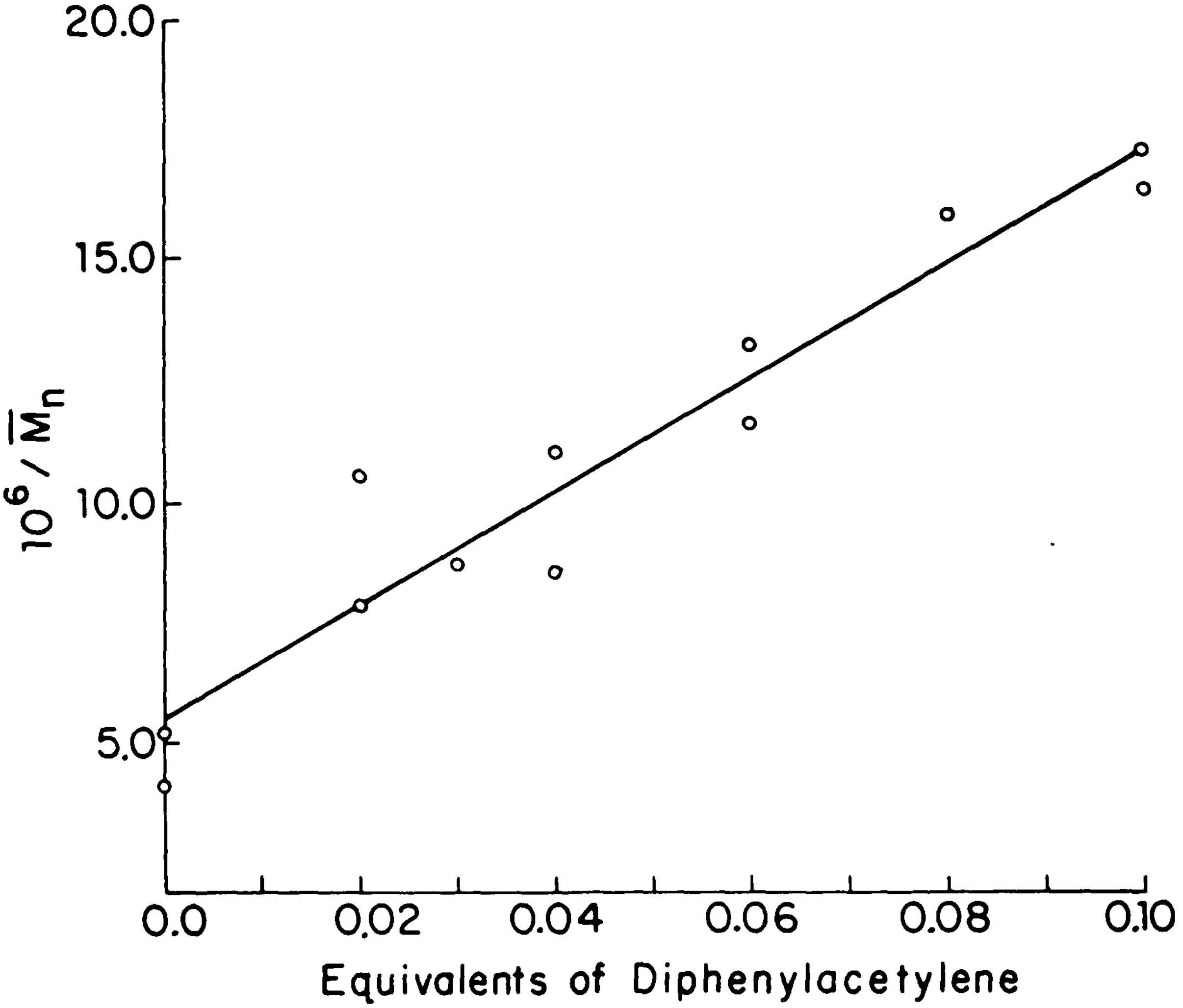

20.0
15.0
10.0
5.0
$10^6/\overline{M}_n$
0.0
0.02
0.04
0.06
0.08
0.10
Equivalents of Diphenylacetylene

Table S-3. $y = 3.84$

Eq. Diphenylacetylene [a]	0.00	0.02	0.04	0.06	0.08	0.20
UV Area High MW [b-1]	1249.3±6.5	2222.8±82.6	2540.7±6.3	2993.0±78.6	2657.5±30.2	2881.6±18.9
UV Area Low MW [b-2]	448.2±13.2	1301.4±99.6	1603.5±54.7	2232.6±121.1	2194.5±55.3	3603.0±151.9
PPA injected (mg) [b-3]	0.00760	0.01576	0.01856	0.0234	0.02172	0.02904
Conc. (mg/mL) [c-1]	0.73	0.78	0.80	0.86	0.79	0.79
Injection Volume (mL) [c-2]	0.3	0.3	0.3	0.3	0.3	0.3
Polymer Injected (mg) [c-3]	0.219	0.234	0.240	0.258	0.237	0.237
PPA (mg/mg polymer) [c-4]	0.0347	0.0674	0.0773	0.0907	0.0916	0.1225
Polymer yield (mg) [d-1]	114.55	73.50	67.35	52.80	49.05	32.30
PPA yield (mg) [d-2]	3.97	4.95	5.21	4.79	4.49	3.96
Yield (%) PPA total [d-3]	35.6	44.3	46.7	42.9	40.2	35.5
UVHA/UVLA [e-1]	2.79±0.10	1.73±0.20	1.59±0.05	1.35±0.11	1.21±0.02	0.80±0.04
PPA on High MW (mg) [e-2]	2.92	3.14	3.20	2.75	2.46	1.76
PPA on Low MW (mg) [e-3]	1.05	1.81	2.01	2.04	2.03	2.20
Polypentenamer (mg) [f-1]	110.58	68.55	62.14	48.01	44.56	28.34
$10^{-3}\ \overline{M}_n$ (High MW) [f-2]	90.5±0.9	62.5±7.1	55.7±3.3	55.4±2.9	52.6±0.9	40.5±1.0
$10^{6}\ N_c$ (mole) [f-3]	1.25	1.15	1.17	0.92	0.89	0.74
$10^{-3}\ \overline{M}_w$ (Low MW) [g-1]	5.47±0.40	7.67±1.93	7.97±0.40	10.00±1.07	10.73±0.67	7.36±0.03
$10^{-3}\ \overline{M}_n$ (Low MW) [g-2]	1.57±0.13	3.13±0.67	3.13±0.27	4.00±0.4	4.53±0.80	2.47±0.22
$10^{6}\ N_c$ (mole) [g-3]	0.57	0.59	0.65	0.51	0.45	0.49
$10^{-3}\ \overline{M}_n$ PPA on High MW [h]	2.34	2.73	2.74	2.99	2.76	2.34
Yield (%) Polypentenamer [i]	24.5	17.7	16.1	12.4	11.5	7.4
RI Area High MW (x 1) [j-1]	2643.9±167.0	2547.6±92.4	2671.5±93.5	2956.7±21.1	2452.0±138.1	2495.7±47.2
Wt. Polypentenamer/wt. PPA High [j-2]	36.1	19.6	18.0	16.9	15.7	14.8
$10^{-3}\ \overline{M}_w$ High [k]	162.1±1.9	98.6±11.1	89.7±6.0	90.5±1.9	81.4±1.4	61.6±0.2
Av. % Change in C≡C/C=C [ℓ]	-4.9	-16.1	-18.2	-17.4	-16.2	-15.2

Table S-4. $y = 3.84$

Eq. Diphenylacetylene [a]	0.00	0.02	0.04	0.06	0.08	0.10	0.20
UV Area High MW [b-1]	5933.58	14565.64	16805.4	21170.0	14031.8	11631.08	13129.2
UV Area Low MW [b-2]	1851.74	8593.64	9994.32	8660.8	8514.8	6966.2	7362.5
PPA injected (mg) [b-3]	0.00871	0.02592	0.02999	0.03338	0.02523	0.02081	0.02293
Conc. (mg/mL) [c-1]	0.72	0.75	0.81	0.75	0.76	0.78	0.80
Injection Volume (mL) [c-2]	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Polymer Injected (mg) [c-3]	0.216	0.225	0.243	0.225	0.228	0.234	0.240
PPA (mg/mg polymer) [c-4]	0.0403	0.1152	0.1234	0.1484	0.1107	0.0889	0.0955
Polymer yield (mg) [d-1]	115.80	49.05	47.40	30.15	50.80	43.90	30.95
PPA yield (mg) [d-2]	4.67	5.65	5.85	4.47	5.62	3.90	2.96
Yield (%) PPA total [d-3]	41.9	50.7	52.5	40.1	50.4	35.0	26.5
UVHA/UVLA [e-1]	2.848±0.356	1.810±0.115	1.818±0.137	2.223±0.221	1.676±0.028	1.764±0.094	1.643±0.150
PPA on High MW (mg) [e-2]	3.46	3.64	3.77	3.08	3.52	2.49	1.64
PPA on Low MW (mg) [e-3]	1.21	2.01	2.08	1.39	2.10	1.41	1.32
Polypentenamer (mg) [f-1]	111.13	43.40	41.55	25.68	45.18	40.00	27.99
$10^{-3}\bar{M}_n$ (High MW) [f-2]	72.83±6.25	33.56±4.07	36.62±2.75	28.8±3.19	36.37±3.32	42.25±4.71	32.50±2.45
$10^{6} N_c$ (mole) [f-3]	1.573	1.402	1.238	0.999	1.339	1.006	0.918
$10^{-3}\bar{M}_w$ (Low MW) [g-1]	4.59±0.4	6.73±0.16	6.96±0.25	6.01±0.79	6.69±0.03	6.65±0.13	6.36±0.81
$10^{-3}\bar{M}_n$ (Low MW) [g-2]	1.71±0.10	2.91±0.13	3.00±0.13	2.90±0.55	2.78±0.09	2.88±0.01	2.51±0.35
$10^{6} N_p$ (mole) [g-3]	0.710	0.692	0.693	0.460	0.756	0.489	0.446
$10^{-3}\bar{M}_n$ PPA on High MW [h]	2.20	2.60	3.05	3.08	2.63	2.48	2.20
Yield (%) Polypentenamer [i]	28.7	11.2	10.7	6.6	11.7	10.3	7.2
RI Area High MW (x 1) [j-1]	2646.24	2815.22	3064.71	3003.88	2834.04	2706.66	2498.54
Wt. Polypentenamer/wt. PPA High [j-2]	31.65	13.87	13.68	10.13	14.79	15.67	13.16
$10^{-3}\bar{M}_w$ High [k]	130.81±5.42	63.28±1.75	64.06±6.49	55.11±4.02	65.29±6.83	69.62±7.14	60.05±6.32
Av. % Change in C≡C/C=C [l]	-9.2	-22.2	-23.4	-17.9	-21.9	-13.7	-10.4

Table S-5. $y = 1.28$

Eq. Diphenylacetylene [a]	0.00	0.02	0.03	0.04	0.06	0.08	0.10
UV Area High MW [b-1]	1053.57±73.80	2020.10±68.21	2049.06±46.69	1627.51±43.77	2283.21±178.67	4446.01±100.94	3505.13±198.[illegible]
UV Area Low MW [b-2]	229.63±39.11	479.30±25.58	858.80±71.04	617.56±15.82	887.30± 22.86	2187.99± 51.5	1069.58±22.[illegible]
PPA injected (mg) [b-3]	0.00144	0.00280	0.00325	0.00251	0.00355	0.00742	0.00512
Conc. (mg/mL) [c-1]	0.76	0.80	0.63	0.59	0.73	0.90	0.87
Injection Volume (mL) [c-2]	0.3	0.3	0.3	0.3	0.3	0.3	0.25
Polymer Injected (mg) [c-3]	0.228	0.240	0.189	0.177	0.219	0.270	0.1275
PPA (mg/mg polymer) [c-4]	0.00632	0.01167	0.01720	0.01418	0.01621	0.02748	0.04016
Polymer yield (mg) [d-1]	127.70	76.50	61.20	57.20	42.55	31.85	25.50
PPA yield (mg) [d-2]	0.81	0.89	1.05	0.81	0.69	0.88	1.02
Yield (%) PPA total [d-3]	21.7	23.9	28.2	21.7	18.5	23.6	27.3
UVHA/UVLA [e-1]	4.67±0.48	4.22±0.08	2.41±0.26	2.64±0.01	2.58±0.27	2.03±0.00	3.29±0.26
PPA on High MW (mg) [e-2]	0.67	0.72	0.74	0.59	0.50	0.59	0.78
PPA on Low MW (mg) [e-3]	0.14	0.17	0.31	0.22	0.19	0.29	0.24
Polypentenamer (mg) [f-1]	126.89	75.61	60.15	56.39	41.86	30.97	24.48
$10^{-3}\ \bar{M}_n$ (High MW) [f-2]	235.77±19.36	126.10±13.56	113.48±3.48	115.85±5.21	85.33±7.20	62.74±3.24	60.63±1.1[illegible]
$10^6\ N_c$ (mole) [f-3]	0.541	0.605	0.537	0.492	0.496	0.503	0.417
$10^{-3}\ \bar{M}_w$ (Low MW) [g-1]	12.45±3.53	8.71±0.01	9.87±0.51	9.43±0.97	9.59±0.28	9.61±0.97	8.95±1.48
$10^{-3}\ \bar{M}_n$ (Low MW) [g-2]	4.57±1.58	3.09±0.17	3.70±0.12	4.53±0.53	4.08±0.78	4.13±0.89	3.74±0.82
$10^6\ N_p$ (mole) [g-3]	0.030	0.056	0.084	0.048	0.047	0.071	0.065
$10^{-3}\ \bar{M}_n$ PPA on High MW [h]	1.24	1.19	1.38	1.20	1.01	1.17	1.87
Yield (%) Polypentenamer [i]	32.8	19.5	15.5	14.6	10.8	8.0	6.3
RI Area High MW (x 1) [j-1]	2597.62±106.37	2483.1[illegible]±30.54	2201.65±81.98	1646.66±149.57	20[illegible]3.33±272.87	3116.45±22.62	2395.7[illegible]
Wt. Polypentenamer/wt. PPA High [j-2]	169.5	84.0	73.5	69.0	61.0	48.1	46.9
$10^{-3}\ \bar{M}_w$ High [k]	470.18±15.82	240.92±6.55	217.61±6.66	211.78±4.05	168.56±1.39	127.97±1.44	112.14±0.[illegible]
Av. % Change in C≡C/C=C [l]	+8.3	-2.7	-7.5	-4.2	-4.3	-8.5	-11.2

Table S-6. y = 1.28

Eq. Diphenylacetylene [a]	0.0	0.1	0.2	0.3	0.4	1.0
UV Area High MW [b-1]	1205.79±61.36	1273.00±58.14	1163.78±32.38	2770.34±159.57	3823.45±323.47	11090.5
UV Area Low MW [b-2]	145.20±1.55	183.61±38.87	144.92±9.39	1312.96±147.85	4231.98±248.08	30200.6
PPA injected (mg) [b-3]	0.00151	0.00163	0.00146	0.00457	0.00901	0.04620
Conc. (mg/mL) [c-1]	0.82	0.47	0.42	0.47	1.16	0.97
Injection Volume (mL) [c-2]	0.3	0.5	0.5	0.5	0.2	0.2
Polymer Injected (mg) [c-3]	0.246	0.235	0.210	0.235	0.232	0.194
PPA (mg/mg polymer) [c-4]	0.00614	0.00694	0.00695	0.01944	0.03884	0.23814
Polymer yield (mg) [d-1]	262.30	194.05	170.35	54.10	23.20	4.85
PPA yield (mg) [d-2]	1.61	1.35	1.18	1.05	0.90	1.15
Yield (%) PPA total [d-3]	43.2	36.2	31.6	28.2	24.1	30.8
UVHA/UVLA [e-1]	8.31±0.51	7.19±1.21	8.08±0.75	2.13±0.12	0.91±0.03	0.37
PPA on High MW (mg) [e-2]	1.44	1.19	1.05	0.72	0.43	0.31
PPA on Low MW (mg) [e-3]	0.17	0.16	0.13	0.33	0.47	0.84
Polypentenamer (mg) [f-1]	260.69	192.70	169.17	53.05	22.50	3.70
10^{-3} $\bar{M}_n$ (High MW) [f-2]	210.7±1.3	195.4±1.0	169.7±6.4	88.2±2.9	56.6±1.4	20.3
10^{6} N_c (mole) [f-3]	1.244	0.992	1.003	0.610	0.402	0.198
10^{-3} $\bar{M}_w$ (Low MW) [g-1]	8.17±0.82	8.30±1.47	8.34±1.28	8.93±0.53	10.78±0.36	8.45
10^{-3} $\bar{M}_n$ (Low MW) [g-2]	2.83±0.74	2.23±0.1	2.50±0.02	3.23±0.07	3.87±0.12	2.94
10^{6} N_p (mole) [g-3]	0.06	0.072	0.053	0.102	0.122	0.285
10^{-3} $\bar{M}_n$ PPA on High MW [h]	1.16	1.20	1.05	1.18	1.07	1.57
Yield (%) Polypentenamer [i]	67.4	49.8	43.7	13.7	5.8	1.0
RI Area High MW (x 1) [j-1]	2673.46±55.86	2403.95±120.97	2265.23±57.2	2410.14±27.17	1891.53±122.17	1133.24
Wt. Polypentenamer/wt. PPA High [j-2]	151.5	128.2	133.3	59.2	33.9	7.0
10^{-3} $\bar{M}_w$ High [k]	470.1±13.0	431.4±4.6	337±0.8	154.6±0.4	92.9±0.0	28.5
Av. % Change in C≡C/C=C [l]	+37.1	+13.6	+10.8	-8.4	-9.7	-15.0

Footnotes

[a] The number of equivalents, x, of diphenylacetylene in equation 3.

[b-1] The area (arbitrary units) under the high molecular weight gpc peak as monitored by the UV light absorption at 254 nm.

[b-2] The area (arbitrary units) under the low molecular weight gpc peak as monitored by the UV light absorption at 254 nm.

[b-3] The weight of PPA injected into the gel permeation chromatograph for each analysis. This is 100n[(b-1) + (b-2)]/8.94 x 10^5, where n is the instrument sensitivity setting, 0.04 for the experiments in Table S-3 and 0.01 for the others. The actual change in instrument sensitivity was established separately to be within 2% of the nominal change.

[c-1] The weight of total polymer per mL of the THF solution used for the gpc analysis.

[c-2] The volume of solution injected for each gpc analysis.

[c-3] The weight of polymer in each gpc injection. This is (c-1) x (c-2).

[c-4] The weight of PPA in each milligram of polymer. This is (b-3)/(c-3).

[d-1] The total weight of polymer isolated.

[d-2] The weight of all PPA in the whole polymer sample. This is (c-4) x (d-1).

[d-3] The yield of all PPA. This is 100 x (d-2)/2.90y.

[e-1] The ratio of the areas under the high- and low-molecular weight gpc peak (UV trace). The scatter is listed of measurements on two injections.

e-2 The weight of PPA on the high molecular weight chain. This is [(d-2) x (e-1)]/[(e-1) + 1].

e-3 The weight of PPA that is not attached to polypentenamer chains. This is (d-2) - (e-2).

f-1 The yield of polypentenamer in mg. This is (d-1) - (d-2).

f-2 The number average molecular weight of the high molecular weight peak (RI measurements). This is one half the molecular weight according to polystyrene standards.

f-3 The number of high molecular weight chains. This is [(f-1) + (e-2)]/(f-2).

g-1 The weight average molecular weights of the low molecular weight gpc peaks as analyzed using the UV trace. The weights are those according to polystyrene standards divided by 1.5.

g-2 The number average molecular weights of the low molecular weight gpc peaks, analyzed as in note g-1.

g-3 The number of chains of PPA that is not attached to polypentenamer. This is (e-3)/(g-2).

h $\bar{M}_n$ of the PPA on the high molecular weight chain. This is (e-2)/(f-3).

i The yield of polypentenamer. This is (100)(f-1)/387.

j-1 The area (arbitrary units) under the high molecular weight gpc peak as monitored by the refractive index change.

j-2 The weight of polypentenamer divided by the weight of poly(phenylacetylene) attached to the polypentenamer. This is (j-1)(68.5)/100n(b-1), where n is defined in note b-3.

k The weight average molecular weights of the high molecular weight chains, measured as in note f-2.

[ℓ] The average change in the ratio of phenylacetylene and cyclopentene during the experiments. This is $100[(i)-(d-3)]/[2(100-(i))]$.

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