The Radiation Induced Polymerization of Cyclophosphazene Trimers

Vivian T. Stannett

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Hexachlorophosphazene was irradiated in bulk and in solution after various methods of purification. When rigorously dried and purified good yields of polymer were obtained. Poor reproducibility was found in the bulk but reasonably good results were obtained in decalin solution. The best yields and highest molecular weights were obtained after the addition of small amounts of the bulky electron acceptor pyromellitic dianhydride. Further details of the work follow.

Hexachlorocyclotriphosphazene was purified by recrystallization for various times from dried heptane. Finally the trimer was dried in the melt over rigorously baked out barium oxide. The monomer was then transferred to ampules or the NMR tubes for radiation and subsequent determination of the polymer content.
The solvent, decalin, and the additive pyromellitic dianhydride were also rigorously purified and dried. Details of all the experimental procedures are contained in the body of this report.

Since the trimer is known to polymerize thermally, control experiments were conducted in each case for the same times and temperatures used for the radiation studies. No thermal polymerization took place with the highly purified trimer at the temperatures used.

In bulk, the superdried trimer polymerized in the solid state but only slightly more than the earlier reported experiments with less rigorously purified and dried material. In contrast, however, the liquid was polymerized to reasonable yields, up to 35% at 195°C, compared with zero without radiation. Much lower yields were obtained at lower temperatures. The polymer was completely soluble and when converted to the trifluoroethoxy polymer had an intrinsic viscosity of only 0.2 d/l/g. The results were highly irreproducible, however, and this coupled with low molecular weights led to a continuation of the work in solution, with decalin being selected as a suitable solvent.

The results obtained were reasonably reproducible particularly when the conversions to polymer were followed using P^31 NMR in the same tubes. The conversions were found to be linear with dose(time) up to 25% polymerization and about 3/2 order of the rates on the trimer concentration. This would be expected if the trimer participated in the initiation process. The activation energy for polymer formation was found to be about 43 Kcals per mole, comparable with literature values for the BCl_3 catalyzed polymerization and at the lowest end of the 42-57 Kcals per mole for the thermal process. The molecular weights were similar, however, to those found in bulk.

The effect of the addition of a bulky and powerful electron acceptor, pyromellitic dianhydride, was then investigated. In bulk the intrinsic viscosity of the trifluoroethoxy polymer doubled to 0.4 d/l/g and in solution, to 0.6 d/l/g. The latter corresponds to a viscosity average molecular weight of about 500,000, well within the range used industrially. GPC showed the peak value to be 454,000 with a dispersity M_w/M_n of 18.7, no small rings were shown in the NMR studies. The use of bulky electron acceptors had been unsuccessfully attempted in previous work with isobutylene in our group. However, pyromellitic dianhydride was successfully introduced by K. Hayashi with the radiation polymerization of superdried α-methyl styrene and ascribed to ion-pair propagation.

In conclusion, it can be said that the original concept of the research was completely borne out by the studies reported here. More work at higher dose rates and to elucidate the precise mechanism involved is however clearly needed.
THE RADIATION INDUCED POLYMERIZATION OF CYCLOPHOSPHAZENE TRIMERS

FINAL REPORT

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High energy radiation in the form of Cobalt 60 gammas has been explored to initiate the polymerization of hexachlorocyclotriphosphazene. Very early work had shown very low yields of crosslinked polymer when the solid trimer was irradiated. The yield increased steadily as the temperatures increased but dropped to zero at the melting point. Similar behavior had been observed with hexamethylcyclotrisiloxane. It was found subsequently that when the trimer was rigorously dried considerable polymerization took place in the melt. This behavior is consistent with the known supersensitivity of vinyl monomers to unradiation induced cationic polymerization. Since hexachlorocyclotriphosphazene is known to polymerize satisfactorily by a cationic mechanism, the approach of superdrying the trimer in bulk and in solution has been investigated in detail.

The complete results which were quite successful are described in the form of two papers: Part I, concerning irradiation in bulk as the solid and in the melt and Part II, concerning irradiation in decalin solution. These papers will be submitted to "Macromolecules" for publication in the near future.

The Radiation Polymerization of Hexachlorocyclo-
triphosphazene: Part I. In Bulk

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Introduction

The polyphosphazenes represent a unique class of polymers with a completely inorganic backbone. They can be highly flame retardant, biocompatible, chemically resistant and with high temperature resistance. Excellent reviews have been published regarding these polymers [1-5]. Although alternative routes for their synthesis have been presented [5,6] the most attractive still is the polymerization of hexachlorocyclotriphosphazene. High molecular weight products can be obtained, and the chlorines can readily be substituted to give a wide variety of structures. Early work tended to give crosslinked polymers but a real breakthrough occurred when Allcock et al. demonstrated that at lower conversions high molecular
weight soluble poly(dichlorophosphazenes) could be obtained and from which stable poly(organophosphazenes) could be prepared [7-9].

The polymerization of the trimer has been extensively studied over many years. The earlier work has been summarized by Allcock [10], Hagnauer [11] and by Singler et al. [12]. Thermal polymerization at above 220°C has been the main process studied but more recently the use of Lewis acids and other catalysts have been emphasized [13-15]. In all of these studies the strong dependence on temperature and the pernicious influence of even trace amount of impurities has often led to a disconcerting lack of reproducibility. Nevertheless important advances in our understanding of the polymerization mechanism have been made.

It now seems clear that the thermal process is cationic in nature and the initiation step is

\[
\text{Cl} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{N} \quad \text{Cl} \quad \text{Cl} + \text{heat} \rightarrow \text{Cl} \quad \text{P}^+ \quad \text{N} \quad \text{P} \quad \text{Cl} \quad \text{Cl} + \text{Cl}^- \quad (1)
\]

With Lewis acid initiation such as with boron trichloride, much studied by Sennett et al. [13], it is simplest to assume the initiation to be:

\[
\text{Cl} \quad \text{N} \quad \text{Cl} \\
\text{Cl} \quad \text{N} \quad \text{Cl} \quad \text{Cl} + \text{BCl}_3 \rightarrow \text{Cl} \quad \text{P}^+ \quad \text{N} \quad \text{P} \quad \text{Cl} \quad \text{Cl} + \text{BCl}_4^- \quad (2)
\]

However a ring opening mechanism has also been proposed by Sennett et al. [13] together with some supporting evidence. The nature of the end groups in both thermal and catalyzed initiation still appears to be uncertain. The polymerization reaction is, most simply:
High energy radiation is known to initiate cationic polymerization in the solid state and, under extremely pure and dry conditions in the liquid state. Early work by Caglioti et al. [16] and Cordischi et al. [17] showed that polymerization of the trimer to crosslinked materials took place in the solid state with the rate increasing up to the melting point and then dropping to zero. A rather analogous situation was found with hexamethylocyclosiloxane. This monomer was also found to polymerize in the solid but not in the liquid state [18]. More recently, however, when "superdried" substantial and reproducible bulk liquid polymerization was achieved [19-21].

This paper is concerned with the application of this approach to the radiation polymerization of hexachlorocyclotriphosphazene (HCP) in the liquid melt state and in solution. In principle the initiation step could be similar to equation (1) but with radiation rather than heat. Some interesting related results have recently been reported with mass spectra and plasma polymerization [22,23].

Part II will be concerned with radiation induced polymerization in solution.

**Experimental Section**

The hexachlorocyclotriphosphazene used was Phosnic 390 from the Nippon Fine Chemical Co., Ltd. The trimer was first of all recrystallized for various times from heptane which had been dried over CaH₂. The traces of solvent remaining in the monomer, after recrystallization, were removed by repeated sublimation under high vacuum (<10⁻⁵ torr). The superdried monomer was then prepared by drying it over BaO which has been baked under high vacuum (10⁻⁶ torr) at 400 °C for one day. For having a good contact between the monomer...
and the drying agent, the monomer was kept in the liquid state during this procedure. The transfer of samples into ampules or NMR tubes were all carried out under high vacuum by sublimation. Rather elaborate systems with break seals and grease free stopcocks were used throughout. A number of our experiments were carried out in NMR tubes. The progress of the polymerization could be determined rather easily by measuring $^{31}\text{P}$ NMR spectra.

Tetrahydrofuran (THF) (Fisher) was distilled from sodium under N$_2$. The trifluorethanol (Aldrich) was used as received.

The glass vessels used in the experiments had been baked at 400°C under high vacuum (10^{-6} torr). The high polymerization temperature was obtained by using a special oil bath in the chamber of the Co-60 $\gamma$-ray source. The radiation source used was a Gammacell 220, Atomic Energy of Canada Ltd. The dose rate of the $\gamma$-ray source was about 0.1 Mrad./hr.

The conversions was determined in two ways, by subliming out the residual monomer after polymerization or by $^{31}\text{P}$ NMR in which case the polymerization was carried out in sealed NMR tubes. The polymer obtained was converted to the fluoroethoxy polymer using the methods described by Allcock [24].

Results

Initially the early (1962) results obtained by Caglioti et al. [16] in the solid state were repeated with the superdried trimer. The results are shown in Figure 1 together with the best results obtained in the melt and in decalin solution. The early solid state results were only slightly improved by superdrying however polymerization was clearly achieved in the melt and in concentrated solution in dry decalin. Interestingly the effect of superdrying became clear closer to the melting point where some molecular mobility was presumably present. It is believed that, as in the case of the cyclic hexamethylsiloxane trimer the effect of water, or other inhibitors, was minimal due to exclusion by the crystal lattice.

The radiation induced polymerization in the bulk melt was very sensitive to the method and degree of purification and drying. Some typical results are given in Table 1. The highest values obtained were 3.5% per megarad or 0.35% per hour, at 0.1 Mrads per hour, at 195°C. The yields were sharply dependent on temperature and, up to 200°C the corresponding thermal controls gave no polymer. Even at 185°C the conversion to polymer was greatly reduced as shown also in Table 1. The problem of irreproducibility, which became greater at lower temperatures, is clearly illustrated with these results. It can be comfortably assumed that the highest values are the most correct ones [25]. After more than 40 experiments in the melt it was decided that the lack of reproducibility was too severe to enable systematic studies to be undertaken and the work was continued in solution. Also the molecular weights of the polymers were always quite low with intrinsic viscosities of only about 0.2 dl/g., with the corresponding fluoroethoxy polymer, in tetrahydrofuran solution.
Discussion

The initiation of cationic polymerization with high energy radiation is now reasonably well understood. Details as we now know them have been summarized in a number of reviews [26,27].

Briefly:

a. \[ \text{MC} \text{I} \rightarrow \text{MCI}^+ + e^- \]

b. \[ \text{MCI} \rightarrow \text{MCI}^* \]

c. \[ \text{MCI}^+ + e^- \rightarrow \text{MCI}^* \] (geminate recombination)

d. \[ \text{MCI}^* \rightarrow \text{M}^+ + \text{CI}^- \]

e. \[ \text{MCI} \rightarrow \text{M}^+ + e^- f(Y^-) \] (free electrons)

f. \[ \text{MCI} + e^- f \rightarrow \text{M}^+ + \text{Cl}^- \]

Where MCI represents the trimer A in equation (1) and M+ the phosphonium ion B. The formation of B (M+) with radiation is strongly supported by the mass spectrometer data [22]. In liquids M+ is a "free" i.e. unpaired cation and is formed in rather low yields. However such ions are highly reactive and propagate rapidly. The free electrons soon are captured to become, \( Y^- \), anions of largely unknown structure. These are the terminating species and add to the growing cationic chains. This reaction is extremely rapid which accounts for the lack of ion pairs. The kinetics become quite simple and analogous to free radical polymerizations,

\[ R_p = (R_i/k_t)^{1/2} \cdot k_p(M) \]

where \( R_p \) and \( R_i \) are the rates of propagation and initiation and \( k_p \) and \( k_t \) the ionic propagation and termination rate constants.

The stationary state concentration of \( M^+ = (R_i/k_t)^{1/2} \) is much less than in normal free radical polymerizations due to the value of \( k_t \) being so large and, at normal dose rates such as used in this work, is only about \( 10^{-10} \text{ M}^{-1} \). This fact coupled with the high reactivity of unpaired cations leads to the extreme sensitivity of such system to trace of protonic impurities, notably water. These terminate the polymerization by e.g.

\[ \text{M}_n^+ + \text{H}_2\text{O} \rightarrow \text{M}_n + \text{H}_3\text{O}^+ \] (not initiating)

Furthermore \( \text{H}_2\text{O} \) is regenerated by the reaction

\[ \text{H}_3\text{O}^+ + \text{Y}^- \rightarrow \text{H}_2\text{O} + \text{HY} \]
With the polymerization of hexachlorocyclotriphosphazene, initiated thermally or with catalysts, water can also affect the rates as discussed by Allcock et al. [24] and by Sennett et al. [13].

The polymerization reaction also presumably includes chain transfer to monomer, i.e.

\[ M_n^+ + MCl \rightarrow M^+ + M_nCl \]

The HCP trimer has 6 chlorines per monomer unit and transfer could be very much favored over chain growth leading to the low molecular weights observed in this work.

With thermal polymerization the propagation is much increased at the high, e.g. 250°C, temperatures used. The stationary concentration of cations, B in equation (1), could also perhaps be lower than with the radiation initiation. With the catalyzed polymerization presumably ion pairs are involved leading to lower rates of chain transfer and higher molecular weights.

In both bulk and solution free radicals are formed e.g. by reactions d, f, and g, since these can not lead to polymerization they presumably terminate each other by recombination. Unfortunately little work has been reported on the products formed by the radiation of HCP e.g. at lower temperatures when radical reactions only should predominate.

In conclusion it can be said that polymerization in the liquid, molten state has been achieved using rigorous purification and drying procedures. The poor reproducibility and low molecular weights led to a continuation of the work in solution with a better degree of success. The results obtained are presented and discussed in Part II of this series.

Acknowledgement

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References

Figure 1. Radiation polymerization of Hexachlorocyclophosphazene

- Super Dried Monomer, Liu & Stannett
- Bulk Polym. In Melt
- Polym. In 10% Decalin
- Polym. In 10% Decalin
Table 1. Hexachlorocyclotriphosphazene Polymerization in bulk

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</table>

* recrystallized twice

** recrystallized three times
The Radiation Polymerization of Hexachlorocyclo-
triphosphazene: Part II. In Decalin Solution

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Introduction

In Part I hexachlorocyclotriphosphazene was successfully polymerized in the melt to low molecular weight polymers with cobalt-60 gamma radiation [1]. The results were, however, erratic. In this paper results obtained in decalin solution are described and also the effects of an electron acceptor, pyromellitic dianhydride. Decalin had been used in catalyzed polymerizations by Fieldhouse and Fenske [2]. This aliphatic hydrocarbon was judged to be innocuous from a radiation chemistry point of view and to have a high enough boiling point for the polymerization experiments.

Experimental

Decalin (Aldrich) was dried over CaH₂ under vacuum and then over four sodium mirrors. It was dried over one more sodium mirror again just before being introduced into the polymerization tubes.

Pyromellitic dianhydride (Aldrich 99%) was transferred into a glass tube equipped with a Teflon stop cock and a break-seal in a dry box under N₂ and then sealed off under vacuum. It was sublimed once under dynamic vacuum before being transferred into the polymerization tubes by sublimation.

A number of the experiments were performed in NMR tubes. Phosphorus (³¹P) NMR spectra were obtained on an IBM AC-100MHz NMR spectrometer at 90°C within sealed 5 mm NMR tubes in decalin. Aqueous H₃PO₄ was used as an external standard. The intrinsic viscosities of the fluoroethoxy polyphosphazenes were measured with a Ubbelohde type viscometer at 30°C in THF. Gel permeation chromatograms were obtained using a Waters 150C GPC machine at 40°C. The column was a PLGel 10μ Mixed 30 cm column from Polymer Laboratories Inc. THF was used as the elution solvent. Other details are given in the experimental section in part I of this series [1].

Results and Discussion

Some initial results, conducted in separate tubes, are presented in Table 1. It is clear that the condition of preparation, purification and drying have a profound effect on the yield of polymer. Considering first the 195°C results the first three runs were made using the original sample of trimer. Without treatment a yield of 0.2% per hour was obtained and the corresponding thermal control gave zero yield. With decalin saturated with water 0.2% per hour.
yield was also found but the thermal control contributed 0.1% per hour. With 0.05% excess water added the yield was 1.0% per hour but the thermal control gave 0.88% per hour. The latter two runs also gave crosslinked polymer in every case.

Experiments were then conducted, again at 195°C, in which the trimer was recrystallized and dried over BaO under various conditions. It was found that one recrystallization and one BaO drying gave 0.20% per hour of polymer. Three recrystallizations plus one BaO cycle gave 0.22% per hour and two recrystallizations plus two BaO cycles gave 0.11%-0.13% per hour. Finally two recrystallizations plus one BaO drying cycle gave 0.32%-0.36% per hour. These were not only the highest values but also had reasonable reproducibility and were the conditions adopted for all subsequent runs. It should be pointed out that with radiation induced cationic polymerization the highest yields are considered to be the more correct [3]. In all cases the thermal controls, even after 100 hours gave zero polymer. At temperatures below 195°C lower yields were always found, see Table 1, for example samples 16-18.

A number of experiments were conducted using NMR tubes and re-irradiating each time. No post-effect were observed and this method of measuring the yields was adopted. It had also been found to be very effective with cyclic dimethyl siloxane polymerization[4].

Two typical conversion-time curves are presented in Figure 1. The reproducibility was quite good and well within the range of those found in the careful work of Lee, Chu et al. [5,6] with thermal initiation using Raman and laser light scattering. The variations from run to run were attributed to the high sensitivity of the system to impurities and to small amounts of water. The latter problem is compounded with radiation induced cationic polymerizations since these are, themselves, extremely sensitive to traces of water.

Effect of the Monomer Concentration

The internal order of the conversion-time curves fit a 3/2 power dependance of the rate on the monomer concentration. This is illustrated, for example, in Figure 2. It should be pointed out, however, that at the less than 25% conversions studied the data also fitted first order plots. The separate tube experimental results are given in Figure 3. These give a scattered dependance of about 1.7 power. A 3/2 order would be expected if the monomer (trimer) also participates, as is firmly believed, in the initiation process.

Molecular Weights

A number of the polymerizations were converted to the trifluoroethoxy polyphosphazenes and their intrinsic viscosities determined. They were all found to be about 0.2, similar to the bulk products. The reasons for the low values were discussed in Part I [1] and attributed mainly to the high probability of chain transfer to monomer.
It is clear that the radiation approach does yield polymer, the rather low rates are probably the results of the low dose rates used. With high dose rates such as can be obtained with an electron accelerator practically acceptable rates should result.

Effect of Adding an Electron Acceptor

The high reactivity of the free, unpaired, cations undoubtedly leads to extensive chain transfer and rapid termination of the growing chains. It was considered, therefore, that the addition of a bulky efficient electron acceptor would introduce some ion pair, and/or reduced rates of termination of the polymerization and transfer reactions. This had been tried without success many years ago with styrene and isobutylene [7]. More recently, however, Hayashi et al. [8,9] had obtained excellent results with α-methyl styrene and pyromellitic dianhydride. This acceptor has now been tried with hexachlorocyclotriphosphazene in bulk and in decalin solution. In bulk no effect on the rate was obtained but the intrinsic viscosity of the corresponding trifluoroethoxy polymer increased from 0.2 to 0.4. These results are included in Table 2. In decalin solution the results were rather remarkable and are presented in Table 2. The conversion at 195°C increased from 0.36 to 2.25% per hour with the addition of a small amount of pyromellitic dianhydride. Even at 175°C the conversion, in the presence of the electron acceptor increased from about 0.02 to 0.27% per hour.

The temperature dependance is presented as an Arrhenius plot in Figure 4. The activation energy is about 43 Kcals. per mole compared with literature values of 42-57 Kcals. per mole reported for the thermal polymerization[10-12] and 36±4 Kcals. per mole for the BCl₃ catalyzed polymerization [13]. The somewhat lower values found in this and the BCl₃ work presumably reflect the lower activation energies for the initiation step. The energy needed to open the conjugated trimer rings is reflected in the high overall activation energies.

The intrinsic viscosity data is also of considerable interest and is included in Table 2. With 0.14 molar pyromellitic dianhydride present the intrinsic viscosity of the corresponding polymer increased three-fold to 0.6. This corresponds to a weight average molecular weight of about 500,000 [14]. The GPC analysis [Figure 5] showed a unimodal distribution with a wide molecular weight distribution. The NMR analysis showed an absence of any small cyclic oligomers. The M_w/M_n value was 18.7 and the peak value was 454,000. The glass transition temperature was determined with DSC as -66°C and a T(1) at 84 °C. These are the values normally reported for the trifluoroethoxy polymer [15,16].

The considerable effect of the electron acceptor on the polymerization could be due to an increase in the free ion yield due to a reduction in geminal recombination. Considering the magnitude of the effect and also the increase in molecular weight the explanation of Hayashi et al. [8,9] for the introduction of an ion pair mode is more attractive. This suggests for α-methyl styrene that the monomer is an electron donor D which complexes with the electron acceptor A. This results in the formation of an ion pair which has a lower activation energy for the polymerization than the free ions.
acceptor A. The complex DA can be excited by the irradiation, eg. via energy transfer, to form an ion pair. This could now initiate the polymerization and reduce the chain transfer step. In this work the trimer itself could play the same role as α-methyl styrene, i.e. as the donor. Schematically this can be written:

\[
\begin{align*}
D + A & \rightarrow (DA) \text{ complex} \\
D & \rightarrow D^+ \\
D^+ + (DA) & \rightarrow (DA)^+ + D \\
(DA)^+ & \rightarrow (D^+ \cdot - - - A^-) \text{ ion pair} \\
(D^+ \cdot - - - D^-) + M & \rightarrow \text{ ion pair propagation}
\end{align*}
\]

GPC analysis of the polymer obtained shows only one main product with a very widely dispersed molecular weight distribution [Figure 5] which implies that mainly ion pairs are involved.

The absence of small cycle oligomers would also tend to increase the rate since these are known to be much less reactive than the trimer and decrease the rate [17].

Conclusions
1. Conducting the polymerization in decalin gives much better reproducibility than that found with the bulk melt.
2. The addition of pyromellitic dianhydride, a bulky and powerful electron acceptor, gives increased rates and molecular weights. This can be attributed to the introduction of ion-pairs which could delay termination and transfer to monomer.
3. Although the rates are still low increasing the dose rate should bring them up to more practical values.

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References


Figure 1. Radiation polymerization of hexachlorocyclotriphosphazene [HCP] in decalin, (a) [HCP]=2.1 mol./l; (b) [HCP]=2.4 mol./l; T: 195 Deg C; Dose rate: 0.1 Mrad./hr.
Figure 2: Radiation polymerization of HCP at 195 Deg. C
$[M_0] = 2.4 \text{ mol/L}$, solvent: decalin, dose rate: 0.1 Mrad/hr.
Figure 3. Influence of monomer concentration on the reaction rate

Solvent: decalin; T: 195 Deg C; t: 60 hrs; Dose rate: 0.1 Mrad./hr
Figure 4. Solution polymerization of hexachlorocyclotriphosphazene in decalin in presence of pyromellitic dianhydride (PMDA):

Dependence of Rp on Temperature; [PMDA]=0.14 mol./l; [M]o=3 mol./l
Figure 5. GPC chromatogram of trifluoroethoxy polyphosphazene converted from Cl-polymer. Elution solvent: THF, T: 40 Deg C.
Table 1. Influence of HCP and decalin purity
(dose rate: 0.1 Mrad./hr.)

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a) trimer and decalin were used as received
b) decalin was saturated with water
c) 0.05% of water was added in decalin
d) thermal control gave 0.1% per hour of conversion for No. 2 and 0.88% per hour for No. 3. In all other cases there were 0% conversion with the thermal control.
e) crosslinked products were obtained with the radiation and the thermal control samples (No. 2 and 3)
Table 2. Polymerization of hexachlorocyclotriphosphazene in the presence of PMDA in bulk and in decalin solution

<table>
<thead>
<tr>
<th>[M] (mol/l)</th>
<th>[PMDA]a) (mol/l)</th>
<th>T°C b)</th>
<th>t (hrs)</th>
<th>conversion (w%/hr)</th>
<th>intrinsic viscosity (dl/l)</th>
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<td>50</td>
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</table>

a) This indicates only the quantity of PMDA introduced as it is only partly soluble under these conditions.
b) Thermal control gave zero yield at these temperatures.
c) Crude monomer without any purification.