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ORGANOSILANE POLYMERS. II. COPOLYMERS OF ETHYLMETHYL- AND METHY--ETC(U)
DEC 78 J P WESSON, T C WILLIAMS N00014-75-C-1024
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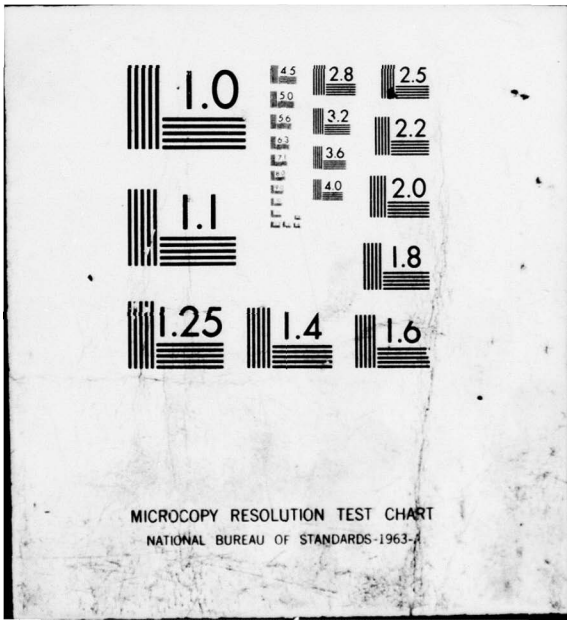
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Random copolymers of ethylmethyl- and methylpropylsilylenes with dimethylsilylene prepared by alkali metal coupling of chlorosilanes were found to have improved solvent solubilities. Some copolymers soluble at ambient temperatures in common solvents were obtained but crystallization behavior was not substantially altered.

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Organosilane Polymers, II: Copolymers of Ethylmethyl- and Methylpropylsilylenes With Dimethylsilylene

by

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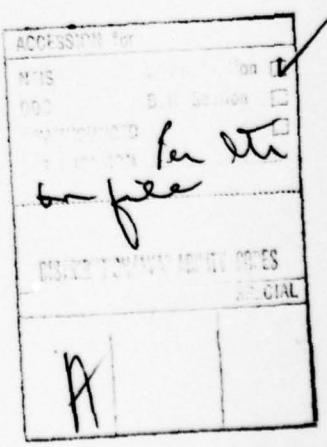
Union Carbide Corporation
Tarrytown, New York 10591

December 1978

INTRODUCTION

Poly(diorganosilylene) higher polymers have received previous attention only as by-product poly(dimethylsilylene) which was found useful as an intermediate in the preparation of cyclic dimethylsilylenes[1,2,3] and more recently as linear higher polymers of dimethylsilylene[4]. The poly(dimethylsilylene) higher polymers are high melting and largely crystalline. They are only soluble at temperatures above about 200°C and are not thermoformable below their decomposition temperatures.

Since one of our goals has been to obtain tractable silylene polymers that are conveniently soluble or thermoformable, we have examined various kinds of copolymers of dimethylsilylene with other diorganosilylenes. This approach stemmed in part from the observation that in some crystalline or crystallizable polymers, the introduction of a few bulky side groups can interfere with chain packing processes thereby depressing crystallization rates and enhancing solubility and thermoforming qualities[5-12]. We report here on the effects of replacing methyl groups with ethyl and propyl groups in random copolymers of dimethylsilylene with ethyl methyl- and methylpropylsilylenes.



EXPERIMENTAL

Monomers

Dimethyldichlorosilane (DMDCS) monomer was purified by treatment with diethyl ether and distillation as described earlier[4]. Ethylmethyldichlorosilane (EMDCS) and methylpropyldichlorosilane (MPDCS) were fractionally distilled under dry nitrogen through a vacuum jacketed column (2.0 x 45.cm) packed with perforated lime glass beads (0.4 cm diam.). Distillation rate was 60 mL hr^{-1} with about 20:1 reflux ratio. Foreruns up to 100°C for EMDCS and up to 125°C for MPDCS were discarded. Product cuts distilling at 100-100.5°C (EMDCS) and 125-125.5°C (MPDCS) were collected and stored under dry nitrogen. After distillation the EMDCS and MPDCS monomers were found to be chromatographically pure.

Copolymers

Random copolymers were prepared by sodium metal dechlorination of mixtures of DMDCS with EMDCS or MPDCS using the methods and precautions previously described[4]. Monomer charges and copolymer yields for typical polymerizations are given in Table I. Copolymers of DMDCS and EMDCS were insoluble in the octane reaction solvent and were recovered directly by filtration. Copolymers of DMDCS and MPDCS ranged from partially to completely soluble in the reaction solvent and were recovered in three fractions:

a) copolymer insoluble in the octane reaction solvent was isolated by filtration,

b) copolymer soluble in octane was stripped of solvent, taken up in THF (100mL) and precipitated by dropwise addition to acetone (300 mL) and dried,

c) copolymer which remained soluble in THF-acetone was solvent stripped to yield viscous oil.

Analytical Methods

Infra-red absorption spectra on the various polymers were obtained with equipment and methods described earlier[4]. Spectra for ethylmethyl- and methylpropylsilylene homopolymers are given for reference in Figures 1 and 2, and absorption band assignments are shown in Tables 2 and 3. Copolymer spectra appeared as typical combinations of the spectra for dimethyl-, ethylmethyl- and methylpropylsilylene homopolymers. Copolymer compositions were calculated from infra-red spectra using absorbances of the $1245cm^{-1}$ (CH_3Si), $1455cm^{-1}$ (C_2H_5Si) and $1460cm^{-1}$ ($n\text{-}C_3H_6Si$) bands[13,14]. Solubilization and precipitation temperatures of the copolymers in perhydrofluorene were determined as described earlier[4]. Molecular weights of polymers insoluble at moderate temperatures were obtained by infra-red methods[4]. Molecular weights of conveniently soluble copolymers were obtained on toluene solutions with a Knauer Vapor Pressure Osmometer at 35 and 65°C; toluene solutions of dodecamethylcyclohexasilane were used as molecular weight references.

RESULTS AND DISCUSSION

Copolymerizations were done by adding chlorosilane monomer mixtures dropwise to sodium metal dispersed in hot, stirred n-octane. The reactions are fast and very exothermic. Suitable precautions are essential to maintain a controlled reaction sequence[4]. The two series of copolymers behave differently during the reaction period. DMS-EMS copolymers were all readily recovered by filtration and worked up to finely divided white powders. With the DMS-MPS system, copolymer solubility in the reaction solvent increased with MPS concentration and it became necessary to recover the products in fractions as described in the Experimental Section. As EMDCS concentration in the monomer mixture is increased, the total yield of copolymer drops steadily to a minimum at about 80 mole-% and then increases somewhat thereafter, Figure 3. In contrast, DMS-MPS copolymer yields are relatively steady at about 65-75% across the composition range. Increased reaction times do not significantly increase yields and part of the sodium metal remains unreacted. Visual inspection of the residual metal suggests that some part of the copolymer coats the metal surface and may then inhibit further reaction. High shear agitation that could scour the metal surface might alter this situation but has not yet been tried. Plots of monomer vs copolymer composition (Figures 4 and 5) indicate that both EMDCS and MPDCS react more slowly than DMDCS particularly at concentrations above about 20 mole %.

Molecular weights were measured as described on the various total polymers and fractions but no significant trends against composition or other experimental variables were noted. In general, $\bar{M}_n$ for the higher polymers varied over the range of 25,000 to 50,000 except for the EMS homopolymer which appeared to be in excess of 100,000.

Solubilization tests were made on octane insoluble copolymers in which the temperatures for complete solution (T_s) and precipitation (T_p) were measured for 2 wt % solutions of copolymer in perhydrofluorene, one of the best solvents for the parent DMS homopolymer so far encountered. Solution and precipitation of the copolymers occurs rather sharply and is generally reproducible within two or three degrees. In the DMS-EMS system, solution temperature (T_s) (Figure 6) decreases rapidly as EMS in the copolymer increases up to about 25 mole % and thereafter decreases slowly to a minimum at about 65 mole %. With DMS-MPS copolymers, the decrease in T_s is also initially very rapid and the extent of depression even more pronounced. At MPS concentrations above about 10 mole %, the copolymers become soluble at ambient temperatures and below and these compositions also become quite soluble in common solvents such as toluene, Figure 7. Thus, silylene copolymers that are soluble at convenient temperatures can be obtained by modifying the parent poly(dimethylsilylene) with relatively small proportions of EMS or MPS units. However, the lack of any significant increase in the solution-precipitation temperature difference (T_s-T_p) suggests that neither the ethyl or propyl group has had any substantial effect on crystallization of the copolymers. This is further borne out in the observation that the copolymers precipitate abruptly from the cooling solution as fine powders with no appreciable tendency for coherent film formation.

To obtain further insight on the effects of structural modifications on copolymer solubility and crystallization a number of block copolymers and short chain branched copolymers are being examined and will be described in future reports.

This work was supported in part by the Office of Naval Research.

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TABLE 1

DIMETHYLSILYLENE COPOLYMERS

Monomer Charged (Mole-%)	Copolymer Yield (wt-%)	Copolymer Composition (Mole-%)
EMDCS:		EMS:
20	74	17
30	67	22
45	48	24
60	44	27
80	23	66
100	74	100
MPDCS:		MPS:
10	73	8
30	66	20
50	67	41
80	46(1)	58
100	78	100

1. Accidental Losses in Work-Up

TABLE 2

INFRA-RED ABSORPTIONS OF

POLY(ETHYLMETHYLSILYENE)

Absorption (cm^{-1})	Assignment
(3450)	(H_2O Stretch)
2950, 2930, 2890, 2870	CH Stretch
1455	CH_3—(—C) Deformation (a)
1420	CH_3 (Si) Deformation (a)
1375	CH_3 (C) Deformation (s)
1245	CH_3 ISi) Deformation (s)
1065	SiOSi
1005	$SiCH_2CH_3$
935	$SiCH_2CH_3$
775, 740	SiC Stretch
690, 670	CH_2 Rocking
650, 610	EtMeSi Rocking

TABLE 3

INFRA-RED ABSORPTIONS OF

POLY(PROPYLMETHYLSILYLENE)

Absorption (cm^{-1})	Assignment
(3450)	(H_2O Stretch)
2950	CH Stretch
2920	
2890	
2870	
(1630)	(H_2O Overtone)
1460	$-CH_2-$(C) Deformation (a)
1450	CH_3-(C) Deformation (a)
1415	CH_3-(Si) Deformation (a)
1375	CH_3 (C) Deformation (s)
1325	CH_2-(C) Deformation (s)
1245	CH_3 (Si) Deformation (s)
1065 (s)	SiOSi
1060	$CH_3CH_2CH_2Si$
985	$CH_3CH_2CH_2Si$
790	SiC Stretch
745	
710	CH_2 Rocking
660	MePrSi Rocking

(s) Shoulder

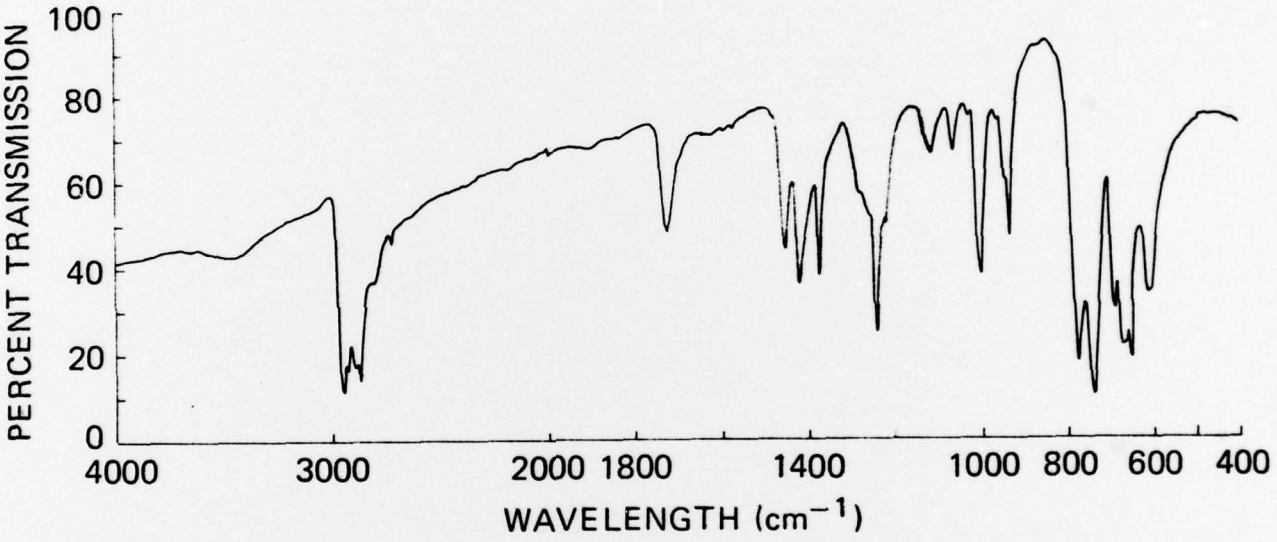

Figure 1.

INFRA-RED ABSORPTION SPECTRUM
POLY (DIMETHYL-Co-ETHYLMETHYLSILYLENE)

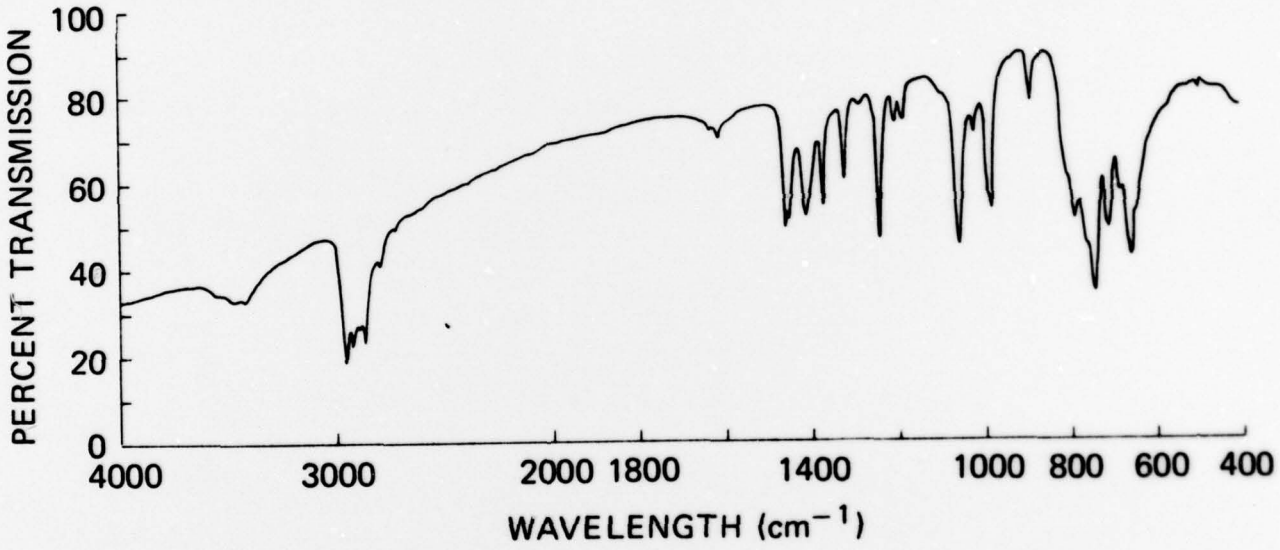

Figure 2.

INFRA-RED ABSORPTION SPECTRUM
POLY (DIMETHYL-Co-METHYLPROPYLSILYLENE)

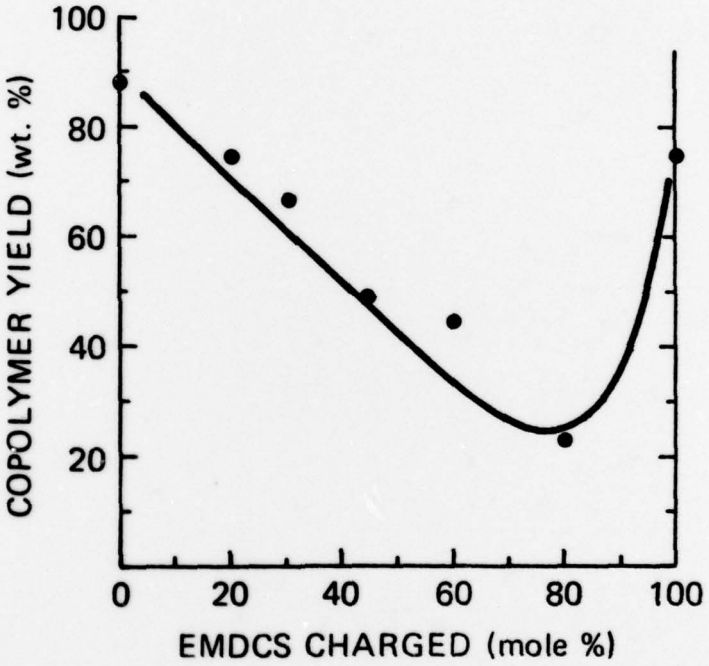

Figure 3.
POLY (DIMETHYL-Co-ETHYLMETHYLSILYLENE) COPOLYMER YIELDS

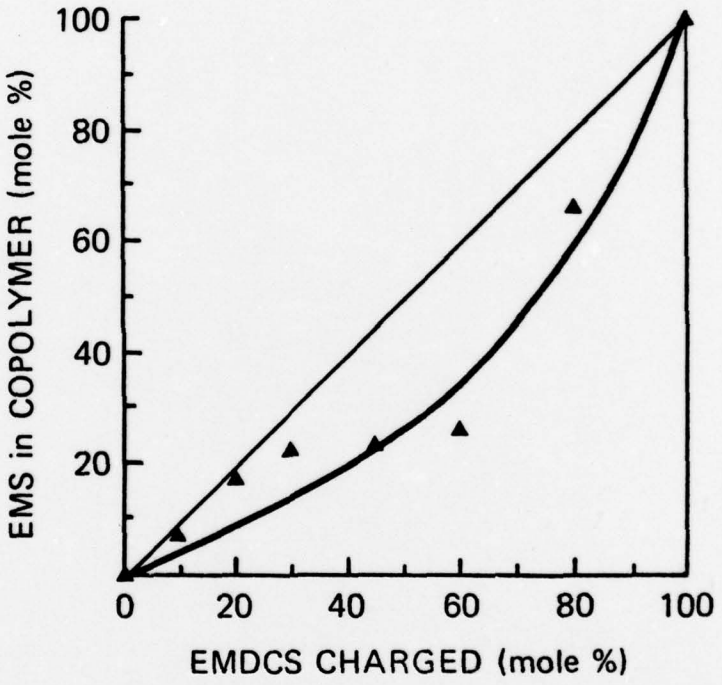

Figure 4.

MONOMER-COPOLYMER COMPOSITION
POLY (DIMETHYL-Co-ETHYLMETHYLSILYLENE)

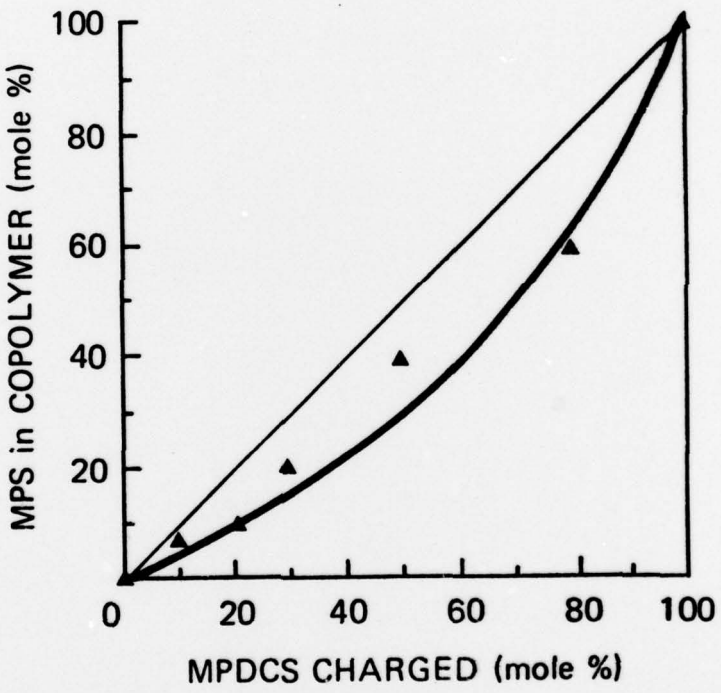

Figure 5.

MONOMER-COPOLYMER COMPOSITION
POLY (DIMETHYL-Co-PROPYLMETHYLSILYLENE)

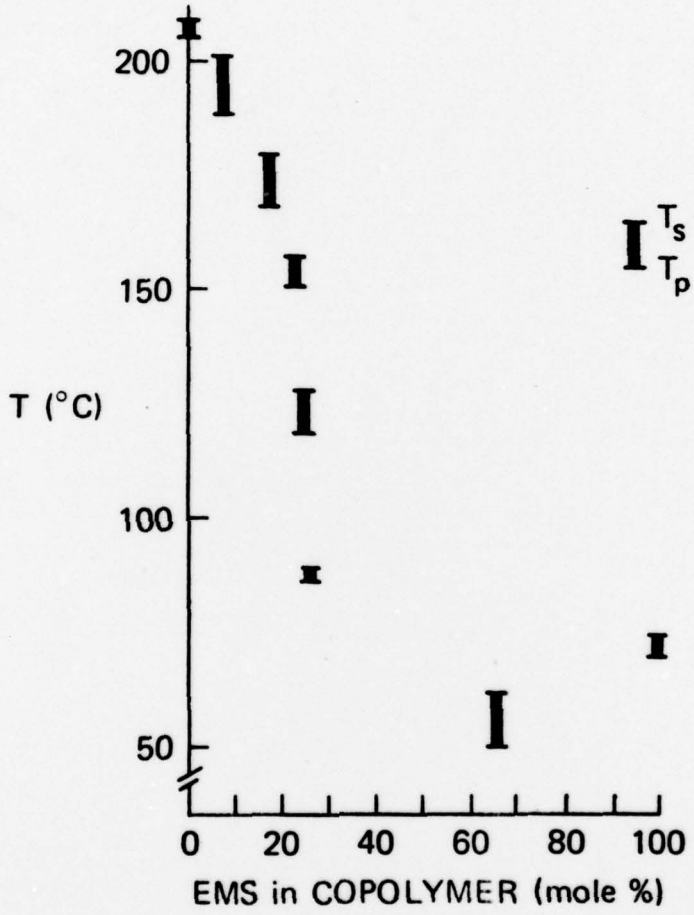

Figure 6.

SOLUTION AND PRECIPITATION TEMPERATURES OF POLY (DIMETHYL-Co-ETHYLMETHYLSILYLENE) IN PERHYDROFLUORENE (2 WT % SOLUTIONS)

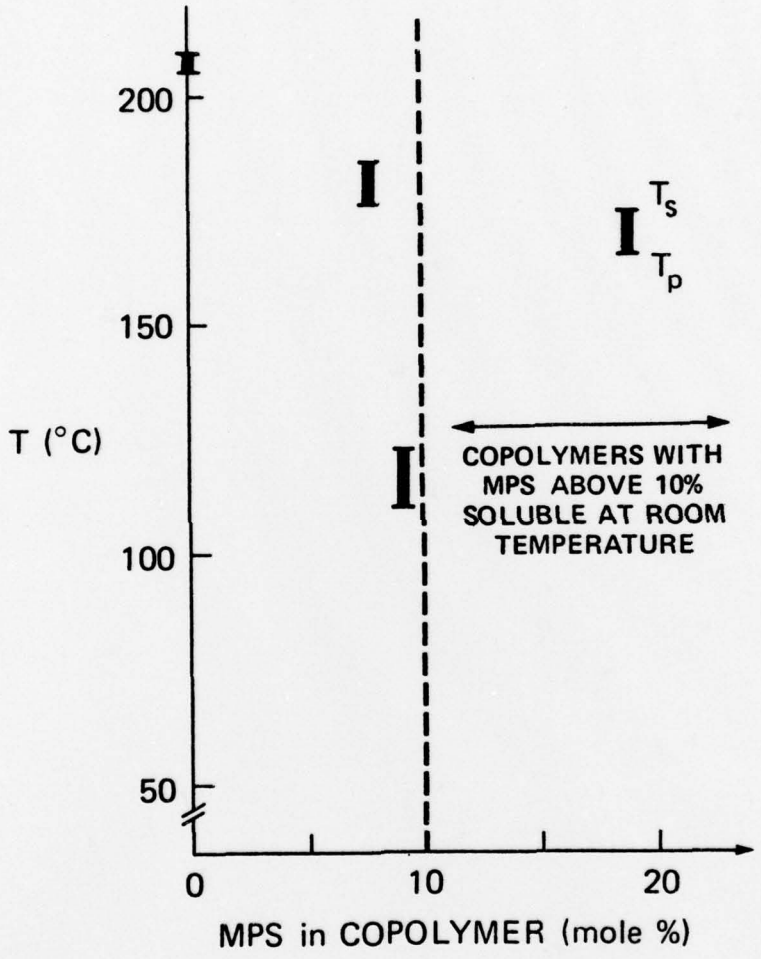

Figure 7.

SOLUTION AND PRECIPITATION TEMPERATURES OF POLY (DIMETHYL-Co-METHYLPROPYLSILYLENE) IN PERHYDROFLUORENE (2 WT % SOLUTIONS)

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