

Anionic Block Copolymerization of Cyclotetrasiloxanes Initiated by 4,4'-Bis(dimethylithiooxylsilyl)diphenyl Ether

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ABSTRACT: The anionic copolymerization of cyclotetrasiloxanes initiated by 4,4'-bis(dimethylithiooxylsilyl)diphenyl ether (BDMOLiPE) was carried out for the preparation of poly(diphenyl-dimethyl-diphenyl)siloxane block copolymers (PMP). To reduce redistribution reaction, the lithium-based dianionic initiator (BDMOLiPE) was first used for the copolymerization of the cyclotetrasiloxane monomers without solvent, with dimethyl formamide (DMF) as a promotor. The cyclotetrasiloxanes used involved octamethylcyclotetrasiloxane (D₄), octaphenylcyclotetrasiloxane (P₄), and tetramethyl-tetramethylcyclotetrasiloxane (V₄). The copolymers obtained were characterized with proton nuclear magnetic resonance spectroscopy, infrared spectroscopy, intrinsic viscosity ($[\eta]$) determination, transmission electron microscopy, and wide-angle X-ray diffraction analysis. The results illustrate that the products should belong to block copolymers but not be too perfect because the block copolymers were scrambled to a certain extent during the copolymerization process. However, we can approximately express them as PMP and PMVP, according to the different order of the feeding in raw materials. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1203–1210, 2001

Key words: 4,4'-bis(dimethylithiooxylsilyl)diphenyl ether; cyclotetrasiloxanes; dimethyl formamide; block copolymerization

INTRODUCTION

The first successful anionic living copolymerization of preparing poly(diphenyl-dimethyl-diphenyl)siloxane triblock copolymers wholly based on siloxane repeating units was carried out by Bostic.^{1, 2} However, the block copolymers do not have good mechanical properties and have to be used by means of chemical crosslinks. As late as the 1980s, Ibemesi³ and Gvozdic⁴ obtained the desired copolymers, which are only soluble at high temperature in a few selective solvents (e.g., di-

phenyl ether), do not need chemical crosslinks, and can be used as thermoplastic elastomers. In these references, the anionic living copolymerization was carried out in diphenyl ether with *n*-BuLi and diphenyl silandiol (DLS) as initiators, tetrahydrofuran (THF) or dimethyl sulfoxide (DMSO) as activating agent, and the trimers of dimethyl and diphenyl siloxane as monomers. In a previous paper,⁵ we reported on the block copolymerization of cyclotetrasiloxanes initiated by *p*-bis(dimethylithiooxylsilyl)benzene (PBDMOLiB), without solvent, and obtained results similar to those of Bostic.^{1, 2} Herein, we report on the copolymerization of cyclotetrasiloxanes initiated by 4,4'-bis(dimethylithiooxylsilyl)diphenyl ether (BDMOLiPE), without solvent and with dimethyl

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Table I Formulation of Materials and Results for Preparing Various Copolymers

Code	P ₄ /D ₄ (wt %)	V ₄ /(P ₄ + D ₄) (wt %)	BDMOHPE/Monomer (wt %)	[η] (mL/g)	Yield (%)
PMP-10	10	0	0.3	92.6	86.1
PMP-40	40	0	0.3	132.1	83.4
PMP-50	50	0	0.3	126.3	80.2
PMVP-10	10	2.0	0.3	83.2	78.0
PMVP-20	20	2.0	0.3	96.8	72.9
PMVP20-10	20	10.0	0.3	96.4	70.5
PMVP-40	40	2.0	0.3	126.4	74.5
PMVP-50	50	2.0	0.3	129.1	81.2

formamide (DMF) as a promotor. Again, we obtained results similar to those of Bostic.^{1, 2} If the copolymerization was carried out in the desired nonequilibrium reaction, according to the order of feeding in raw materials, then the obtained products should belong to triblock copolymers (MPM), polydimethylsiloxane (PDMS) block (the central sequence), and polydiphenylsiloxane (PDPS) block (the outer ones). On the other hand, when a suitable amount of tetramethyl-tetravinylcyclotetrasiloxane (V₄) was added together with octamethylcyclotetrasiloxane (D₄), the dimethylsiloxane segment containing methyl-vinylsiloxanes was formed and, therefore, the PMVP copolymers were obtained. The obtained materials were practically characterized with proton nuclear magnetic spectroscopy (¹H NMR), infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, intrinsic viscosity ([η]) determination, transmission electron microscopy (TEM), and wide-angle X-ray diffraction (WAXD). From these data, we can approximately express them with the aforementioned symbols, although the products are probably not the desired triblock copolymers. It is obvious that polymerization of D₄ and P₄ is more difficult than that of D₃ and P₃, but D₃ and P₃ are not easy to obtain in China. At the same time, we assume that BDMOHPE is more rigid than DLS and does not easily form cyclic compounds. Therefore, BDMOLiPE is probably an effective initiator, using DMF as a promotor, for the block copolymerization of D₄ with P₄ or D₄ and V₄ with P₄.

EXPERIMENTAL

Materials

D₄ was provided by the Chemical Industry Factory of Sandong University. The sample was dried

by refluxing over calcium hydride and distilled prior to use. P₄ was made and treated before use as described previously.⁵ V₄ and BuLi were commercial reagents. DMF and THF were treated according to common practice. Because the obtained products were very difficult to dissolve in toluene or chloroform, the solutions were prepared as follows: the gums were first dissolved under boiling conditions in toluene or CHCl₃, and then the temperature was dropped to room temperature for measurement.

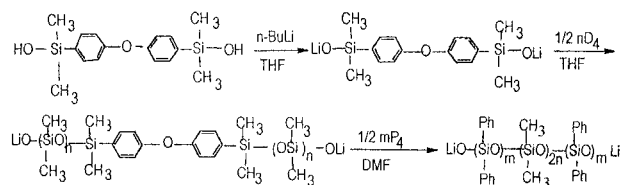
Equipment

¹H NMR spectra were recorded on a FX-90 spectrometer in deuteriochloroform (CDCl₃) using CHCl₃ as internal reference. IR spectra were measured with a Nicolet-5DX spectrometer in the region 400–4000 cm⁻¹ by film coating. UV spectra were examined on a Shimadzu UV-240 spectrometer with 0.0050 ± 0.0005 g/mL of the products solutions in CHCl₃. The intrinsic viscosity values of the polymers were measured with an Ubbelohde viscometer in toluene at 25.00 ± 0.05 °C. The molecular weight distribution was explained with a diagram. The TEM graphs of the copolymers were obtained on a TEM-100C-X2, using toluene as a solvent and pyroxylin film as a supporting film. WAXD was done on a D/MAX-γA X-ray diffractometer.

Because anionic species are easily killed by moisture and O₂, all the glassware equipment was thoroughly cleaned, dried, and assembled under pure N₂. The temperature was uncorrected.

Copolymerization

The required amount of BDMOHPE in 4 mL of THF and *n*-BuLi in *n*-hexane were successively



Scheme 1

introduced into a four-necked round-bottomed flask by a syringe. The flask was equipped with a mechanical stirrer, a separating apparatus of water connected to a reflux condenser equipped with a drying tube of calcium chloride, a nitrogen inlet tube, and a thermometer. The mixture was stirred at room temperature under an atmosphere of dry nitrogen for 20 min to obtain a muddy white liquid. After the directed amount of D_4 was added to the flask, the mixture was heated to 155 °C, THF was given off from the separating apparatus of water, 4 mL of DMF was added into the flask by syringe and, in that moment, the system became clear. The temperature was maintained for 3.0 h to obtain a transparent viscous liquid. After this, while the temperature was dropped ~ 130 °C, a certain amount of P_4 was added and the mixture was stirred until it became milky white. Then the temperature was raised to 180 °C, 2 mL of DMF was added to the system, and the temperature was maintained for 4.0 h to perform the copolymerization. At the end of the polymerization, the system became so viscous that it was very difficult to stir. The reaction mixture was cooled to room temperature, then dissolved in hot (sometimes boiling) toluene, cooled, and precipitated with methanol to yield the copolymers. Finally, the product was dried in a dryer at 80 °C/20 mmHg. The formulation of the materials and results for various copolymers prepared are outlined in Table I.

RESULTS AND DISCUSSION

Copolymerization Process

The copolymerization process is shown in Scheme 1.

BDMOLiPE as a Real Initiator

To testify that BDMOLiPE is a real initiator and takes part in the reaction, we designed the following experiment. Using BDMOHPE (20 wt % of D_4)

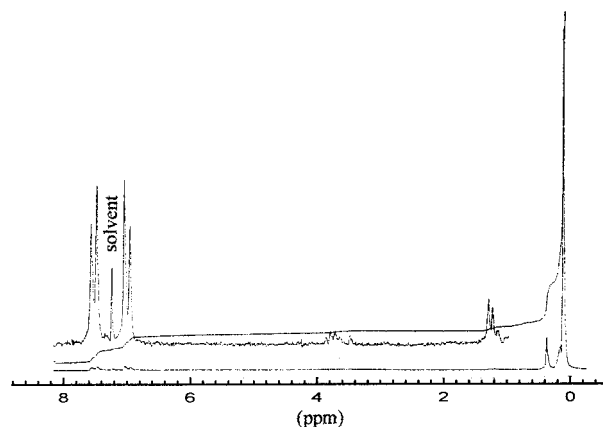


Figure 1 ^1H NMR spectrum of polydimethylsiloxane containing BDMOPE.

and 2 mol of BuLi as initiators, and 2 mL of DMF as promoter, only D_4 was polymerized at 155 °C for 3 h. The product obtained was completely washed with anhydrous alcohol to thoroughly remove nonreactive BDMOLiP. The ^1H NMR spectrum of the obtained polymer, shown in Figure 1, gives the following data: chemical shift (δ , ppm): 7.09(d), 7.56(d), 0.38(s), and 0.08(s). Obviously, these shifts can be assigned to the hydrogen of $-\text{Ph-O-Ph-}$, and SiMe in $(\text{CH}_3)_2\text{SiPh-O-PhSi}(\text{CH}_3)_2$, and $[\text{Si}(\text{CH}_3)_2\text{O}]_n$, respectively. We calculated the integral of the various hydrogen atoms in the ^1H NMR spectrum to estimate the contents of the BDMOPE in the polymer. The estimated result is 19.5%, which is close to the aforementioned 20%. The ^1H NMR spectrum of BDMOHPE is shown in Figure 2. The following chemical shifts (δ , ppm) are evident: 0.36(s, 12H, in MeSi), 1.84(s, 2H, in OH),

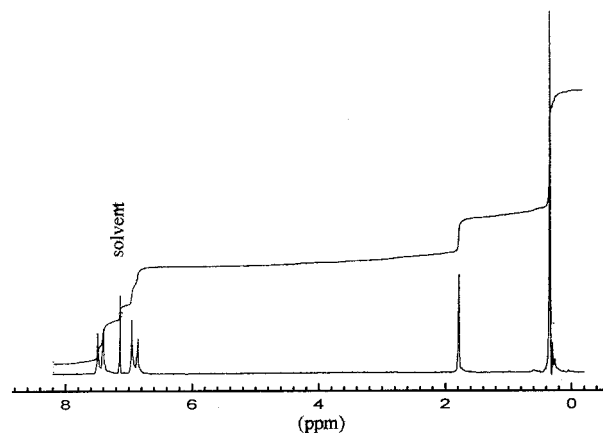


Figure 2 ^1H NMR spectrum of BDMOHPE.

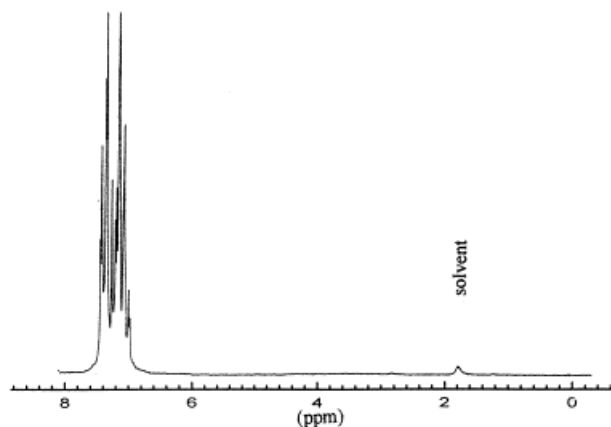


Figure 3 ^1H NMR spectrum of P_4 .

7.01–7.56(quarter, 8H, in $-\text{Ph-O-Ph}-$). Obviously, these results can be explained.

Analysis of the Copolymers with Wave Spectra

The ^1H NMR spectra of P_4 , PMP-50, and PMVP-20-10 are shown in Figures 3–5, respectively. The chemical shifts (δ , ppm) are as follows: 7.20–7.64 ($-\text{Ph-H}$) in Figure 3; 7.33–7.56 ($-\text{Ph-H}$) and 0.04 (Si-CH_3), in Figure 4; and 7.32, 7.56 ($-\text{Ph-H}$), 0.03 (Si-CH_3), and 5.85 (Si-CHCH_2) in Figure 5. The chemical shifts of the phenyl group protons in Figures 4 and 5 are different than those in Figure 3. The groups in Figures 4 and 5 have taken part in the aforementioned polymerization. The ratio of Ph_2SiO chain weight to $(\text{CH}_3)_2\text{SiO}$ chain weight was calculated from the data in Figure 4 as 0.47, which is closed with the value (0.50) of the added P_4 to D_4 . A similar close result was calculated from the data in Figure 5. A peak at ~ 1.84 ap-

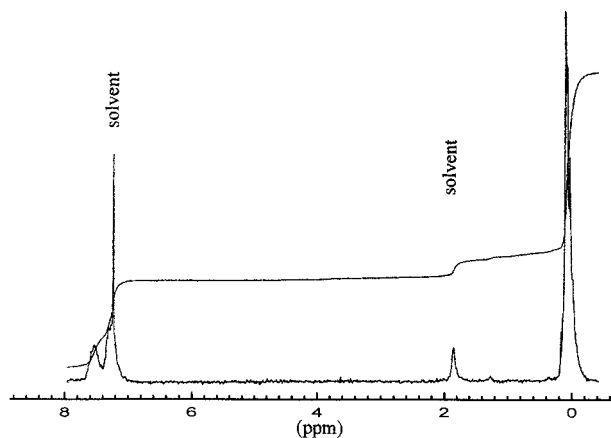


Figure 4 ^1H NMR spectrum of PMP50.

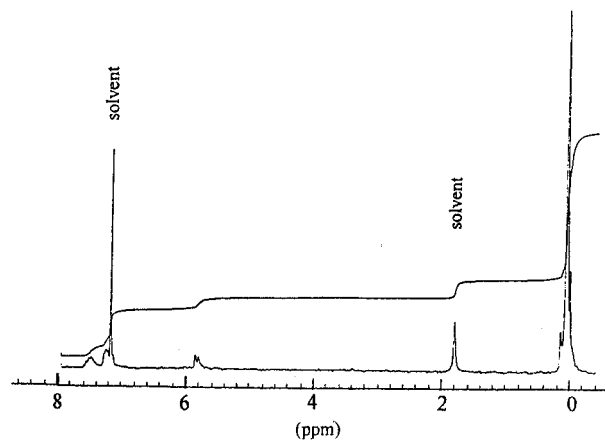


Figure 5 ^1H NMR spectrum of PMVP20-10.

pears in Figures 3–5, which can be assigned to the Si-OH in sample and H-OH in solvent.

The IR spectrum of PMP-40 is shown in Figure 6. This spectrum shows peaks at 698 , 717 , and 742 cm^{-1} (benzene skeleton); 2962 cm^{-1} ($-\text{CH}_2-\text{H}$); 3072 and 3025 cm^{-1} ($-\text{Ph-H}$); and 1023 and 1086 cm^{-1} (SiOSi).

The UV spectra of some of copolymers obtained are shown in Figure 7 (with the following order from bottom to top: PMVP-10, PMVP-20, PMVP-40, PMVP-50). These spectra all show peaks at 233 , 245 , and 271 cm^{-1} , and the peak heights increase with the increasing content of the Ph_2SiO chain element.

Effect of the Initiator Concentration on Intrinsic Viscosity

According to the formulation of PMVP-50 in Table I, the copolymerization and treatment of the obtained products were carried out by the aforemen-

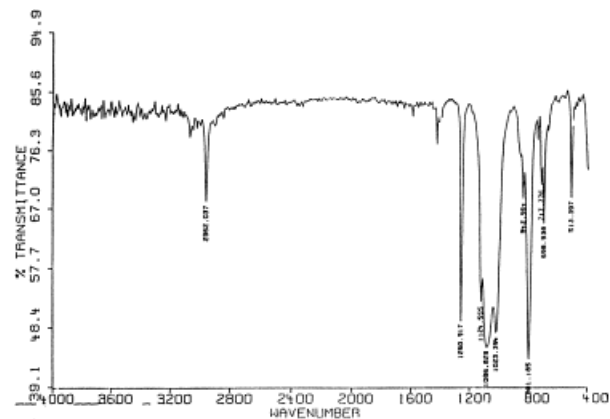


Figure 6 The IR spectrum of PMP40.

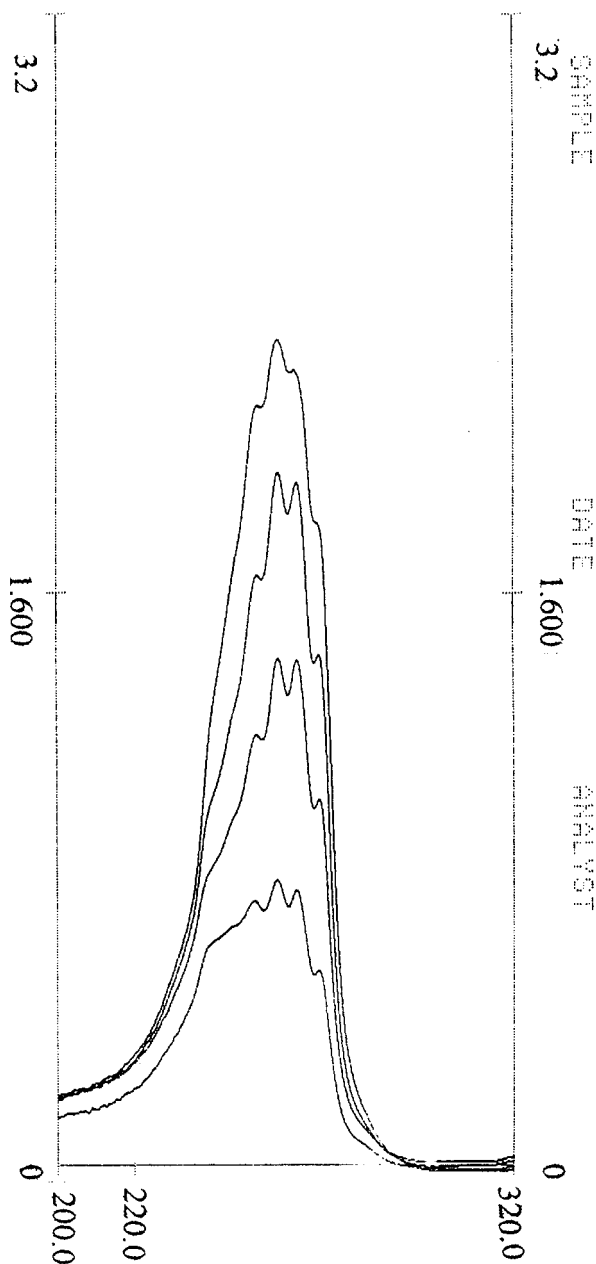


Figure 7 The UV spectra of some copolymers.

tioned process. By changing only the concentration of initiator (BDMOLiPE), the intrinsic viscosity of every product was determined and the results are shown in Table II. When the initiator is <0.10 wt % of the sum of D_4 and P_4 , it is too low for the copolymerization of D_4 with P_4 , but when the initiator is >0.35 wt % of the sum of D_4 and P_4 , the amount of initiator is too high to lead to a high molecular weight. Therefore, an appropriate amount of initiator is between 0.15 and 0.30 wt % of the sum of D_4 and P_4 .

Table II Effect of Amount of Initiator on Intrinsic Viscosity ($[\eta]$)

Amount of Initiator (wt %)	$[\eta]$ (mL/g)
0.10	78.2
0.15	102.7
0.20	116.4
0.25	135.6
0.30	129.1
0.35	84.3
0.40	80.6

Effect of the Polymerization Temperature and Time on Intrinsic Viscosity

According to the formula ratio and polymerization conditions of PMP-50 in Table I, we achieved the copolymerization of D_4 with P_4 , turned out samples every half hour, and dried the samples with the aforementioned method. The intrinsic viscosities of the samples obtained were measured, and the relation of the intrinsic viscosity with polymerization time is shown in Figure 8. The lowest curve was determined at 160°C , and, in view of the unreactiveness of P_4 , at so low a temperature, the intrinsic viscosity does not change after ~ 3 h. However, the middle curve was determined at 180°C , and, in view of the sequential polymerizing of P_4 at that temperature, the intrinsic viscosity does not increase after ~ 5 h. Because of the accompanying crosslink reaction, the top curve, determined at 220°C , is

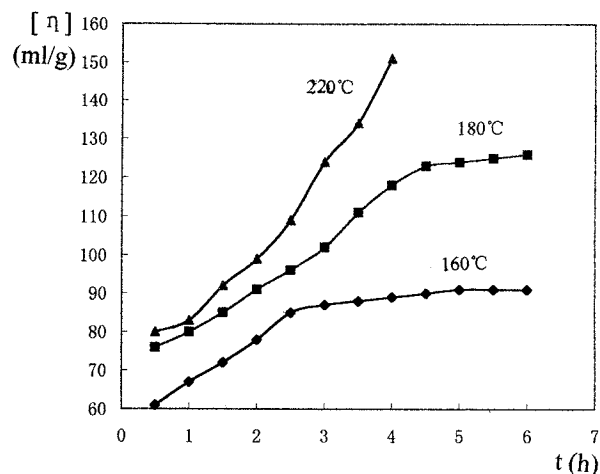


Figure 8 The relation of the intrinsic viscosity with the polymerization temperature and time.

Table III Grading Results for PMVP-20

Grade No.	Weight Fraction (W_f)	Integral Weight Fraction (I_f)	Intrinsic Viscosity [η] (mL/g)
6	0.0648	0.0324	56.3
5	0.1315	0.1306	69.7
4	0.2730	0.3328	90.2
3	0.2642	0.6014	108.5
2	0.1875	0.8273	124.2
1	0.0790	0.9605	139.1

different from the other two curves and almost a straight line.

Molecular Weight Distribution

Even though the obtained samples are difficult to dissolve in some organic solvents, such as toluene, progressive precipitation separation was still used for studying the molecular weight distribution. The samples, PMVP-20 and PMVP-40, were dissolved in boiling toluene, cooled, and then treated with methanol according to a previously published method.⁶ The results shown in Tables III and IV and Figure 9 indicate that the molecular distribution is still comparatively wide for two reasons; first, D_4 and P_4 are not very easy to polymerize and, second, the stirring, particularly after the second material is added, is too difficult to effectively homogenize the reacting substances.

Effect of Promotor on Polymerization

Using only THF as a promotor, we attempted to perform the polymerization of D_4 according to the polymerization conditions just mentioned, but failed. However, the polymerization of V_4 was successful. On the other hand, to prepare the MPM copolymer, we also attempted to perform the polymerization of P_4 using THF or DMF as promotor, but the polymerization of P_4 was not

successful, even at 220 °C. These results illustrate that only THF can promote the polymerization of V_4 , that neither THF nor DMF can promote the polymerization of independent P_4 , but DMF can promote the polymerization of D_4 or the copolymerization of D_4 with P_4 .

Wide-Angle X-ray Diffraction (WAXD)

To determine whether the copolymerization siloxanes exist in the crystal phase and belong to block copolymers we examined PMP-40 by WAXD, and the spectrum is shown in Figure 10. There are two low and wide peaks at 11° and 22° in Figure 10, indicating that PMP-40 possesses some crystals and should belong to a block copolymer.

TEM Analysis

PMP-10 and PMP-40 were examined by TEM and the results are shown in Figures 11 and 12, respectively. These results show that both samples exist in as a two-phase structure; that is, the P segments form a microcrystalline domain as the dispersed phase, and the P segments are dispersed in the continuous phase, which is formed by M segments. A clear phase separation is not evident in the 7200X TEM photo of PMP-10, but is noted at 29000X magnification. In contrast, a clear phase separation is evident in the 7200X

Table IV Grading Results for PMVP-40

Grade No.	Weight Fraction (W_f)	Integral Weight Fraction (I_f)	Intrinsic Viscosity [η] (mL/g)
6	0.1096	0.0548	61.20
5	0.1107	0.1650	76.80
4	0.1650	0.3028	98.6
3	0.2382	0.5044	122.4
2	0.1944	0.7270	138.2
1	0.1758	0.9058	154.7

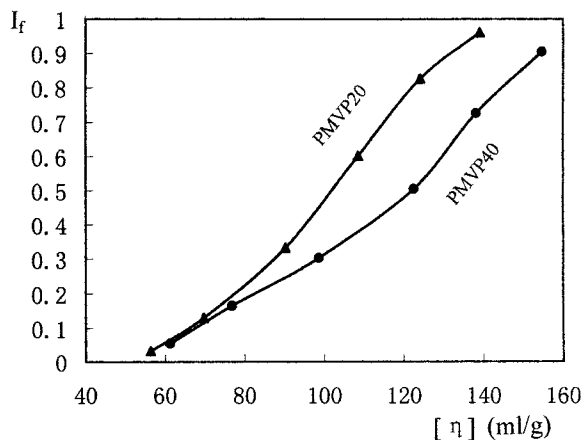


Figure 9 the integral distribution curves of PMVP20 and PMVP40.

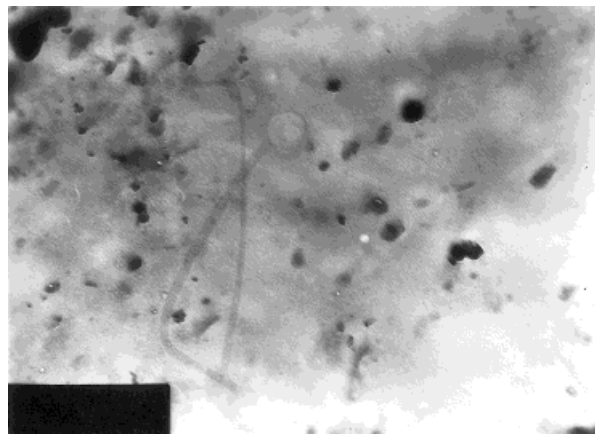


Figure 11 The TEM of PMP10 (29000X).

TEM photo of PMP-40. Thus, we can say that the phase separation degree increases with increasing content of Ph_2SiO chain units.

CONCLUSION

We have attempted the synthesis of a series of PMP and PMVP block copolymers. The copolymers were characterized by ^1H NMR, IR, UV, $[\epsilon]$, TEM, and WAXD techniques. From the appear-

ances of the TEM and WAXD photographs, we find that the products exist as two-phase structures. From the results of the solubility test we find that the products can not be dissolved at room temperature in toluene or chloroform, but can at boiling temperature (though the dissolving is very difficult). Therefore, we consider that the copolymers should belong to block copolymers mainly. Compared with previous results,^{3,4} which indicate that block copolymers were only dissolved at very high temperature in a few selective solvents (e.g., diphenyl ether), our results suggest

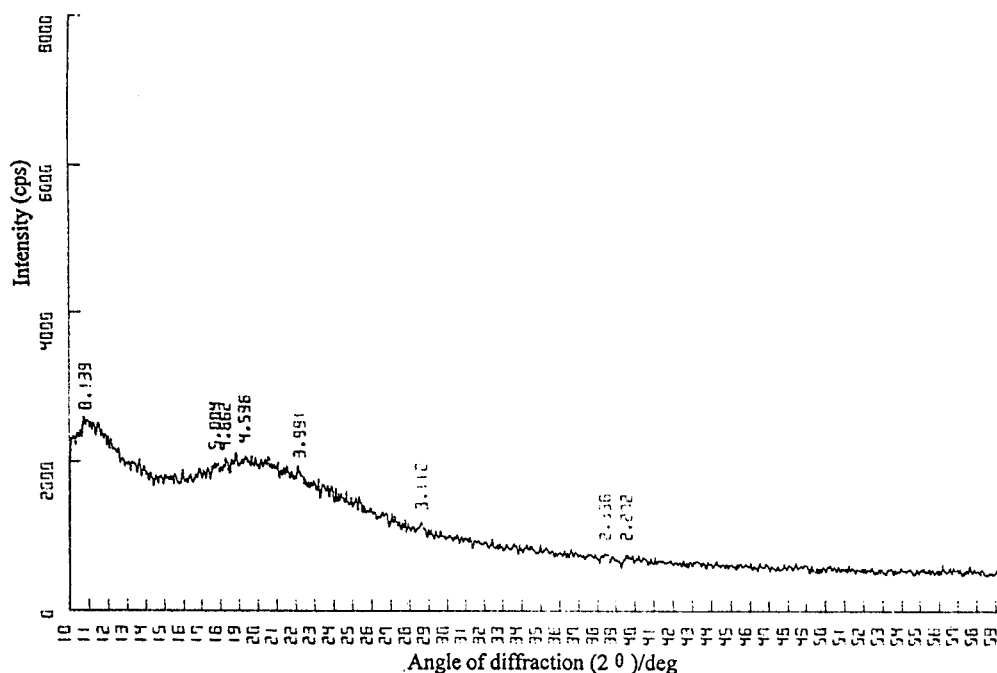


Figure 10 The WAXD spectrum of PMP40.

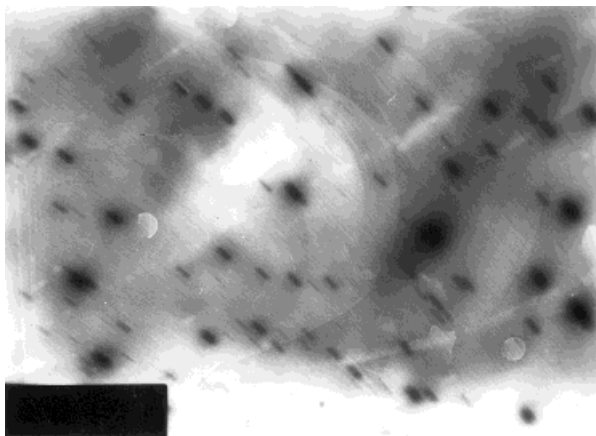


Figure 12 The TEM of PMP40 (7200X).

that our block copolymers were probably disturbed to some extent during the copolymerization process and should not belong to perfect triblock polymers. Instead, they should be approximately expressed as PMP and PMVP according to the different order of feeding in raw materials. Although the hardness of the obtained gums increases with increasing content of Ph_2SiO chain units, the gums are all soft rubbery materials at

room temperature. To date, the polymers still cannot be used as practical thermoplastic elastomers. To help improve the chemical link, a suitable amount of vinyl groups were added to the copolymers. During the investigation process we found that BDMOLiPE is efficient as a initiator of copolymerization for D_4 with P_4 or D_4 , and V_4 with P_4 , and that the presence of DMF is necessary and possesses obvious promotional action. Further investigation is in progress.

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