

## Poly( $\alpha$ -methylstyrene)—Poly(dimethylsiloxane) Block Copolymers

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### Synopsis

Block copolymers were synthesized by the condensation of dihydroxyl-terminated poly( $\alpha$ -methylstyrene) oligomers and bisdimethylamino-terminated poly(dimethylsiloxane) oligomers. Manipulation of block molecular weight produced copolymers ranging in composition from 21% to 73% poly(dimethylsiloxane). Compression moldability was found to be good. Physical properties were dependent upon siloxane content, varying from high modulus, low elongation to low modulus, high elongation materials. High siloxane-content compositions exhibited elastomeric properties due to the two-phase morphology of these systems. Glass transition temperatures were observed as low as  $-120^{\circ}\text{C}$  for the poly(dimethylsiloxane) block and as high as  $+140^{\circ}\text{C}$  for the poly( $\alpha$ -methylstyrene) block. Even higher poly( $\alpha$ -methylstyrene) transition temperatures may be possible by using higher molecular weight oligomers.

### INTRODUCTION

Polystyrene-polybutadiene-polystyrene ABA block copolymers are useful thermoplastic elastomers.<sup>1,2</sup> However, the relatively low glass transition temperature ( $T_g$ ) of polystyrene, i.e.,  $100^{\circ}\text{C}$ ,<sup>3</sup> precludes the use of these materials at elevated temperatures. In addition, their thermal/oxidative stability is limited by the unsaturated polybutadiene block. Block copolymers of poly( $\alpha$ -methylstyrene) (P $\alpha$ MS) and poly(dimethylsiloxane) (PSX) were investigated in order to overcome these two drawbacks, since high molecular weight P $\alpha$ MS is reported to have a  $T_g$  of  $173^{\circ}\text{C}$ ,<sup>4</sup> and silicones are known to exhibit excellent stability.<sup>5</sup>

There are several references in the literature to the synthesis and properties of polystyrene-poly(dimethylsiloxane) block copolymers.<sup>7-14,23-28</sup> These materials have very interesting properties, but their utility is limited by the  $100^{\circ}\text{C}$   $T_g$  of the polystyrene segments. There are two references<sup>6,22</sup> to poly( $\alpha$ -methylstyrene)-poly(dimethylsiloxane) copolymers, but these compositions contain very short segments (tetramers, pentamers). In contrast, the copolymers of the present work contain high molecular weight blocks and accordingly display the properties characteristic of two-phase morphology. The copolymers were synthesized by the condensation of

preformed difunctional P $\alpha$ MS and PSX oligomers bearing mutually reactive endgroups to produce an  $\langle\text{A-B}\rangle_n$  block sequence structure. The two-phase nature of these products is analogous to that of block copolymers reported earlier containing segments of poly(dimethylsiloxane) and segments of condensation polymers such as polycarbonate<sup>30,31,32</sup> and polysulfone.<sup>33</sup>

## EXPERIMENTAL

### Synthesis of Dihydroxyl-Terminated $\alpha$ -Methylstyrene Oligomers

This synthesis was carried out in nonaqueous dispersion medium<sup>29</sup> in order to avoid the large viscosity build-up (due to association) in the ethylene oxide capping step which is characteristic of this reaction when carried out in solution.<sup>20,21</sup> The dialkoxide ion was terminated with acid before exposure to air in order to prevent side reactions leading to endgroups other than —OH.<sup>21</sup> Oligomer molecular weight was varied by changing the monomer/initiator ratio. A typical synthesis was as follows:

A 2-liter four-neck flask equipped with a mechanical stirrer, two gas inlets, a gas exit, a serum stopper, and a thermometer was charged with 800 ml of normal heptane, 300 ml of  $\alpha$ -methylstyrene, 20 ml of  $\alpha$ MST containing 50 g/l. poly(vinyl ethyl ether), and 10 ml of a sodium dispersion containing 40 wt-% Na metal in mineral oil. At room temperature, and with good stirring, 60 ml of tetrahydrofuran was introduced with a hypodermic syringe. Within a few minutes, the solution became dark purple. The solution was kept at 30°C for 15 min, then cooled rapidly with an ice/acetone bath to 0°C, and kept at that temperature for another 15 min. Polymerization occurred, producing a dispersion of poly( $\alpha$ -methylstyrene). Ethylene oxide was bubbled into the dispersion until the dark-purple color of the living anion discharged completely. The temperature was permitted to rise during this operation to +5°C. When the dispersion was colorless, 30 ml of concentrated acetic acid was added. The addition of the acetic acid caused coagulation of the polymer. At this point, stirring was discontinued and the polymer was permitted to settle to the bottom of the flask. With a hypodermic syringe, 400 ml of diluent was removed from the flask and replaced with 500 ml of tetrahydrofuran. The polymer dissolved, and the solution was stirred at room temperature for another 10 min. Finally, the solution was precipitated with methyl alcohol, washed twice with normal heptane, and dried in vacuum at 100°C to produce 180 g of polymer. The polymer had an R. V. of 0.09 (0.2 g/dl in toluene at 25°C). The  $\bar{M}_n$ , as determined by the stoichiometry of the block copolymer reaction was 7,300.

### Bisdimethylamino-Terminated Poly(dimethylsiloxane) Oligomers

These were provided by Mr. T. C. Williams of the Silicones Department of Union Carbide Corporation. Oligomer molecular weight ( $\bar{M}_n$ ) is determined by potentiometric titration of the amine endgroups. The PSX oligomers used to synthesize copolymers I, II, III, IV, and V (see

Table I) had the following  $(\text{CH}_3)_2\text{N}$  contents and calculated  $\bar{M}_n$  values: 1.68% (5,200), 5.15% (1,700), 1.63% (5,400), 0.88% (10,000), and 0.43% (20,500), respectively.

### Synthesis of P $\alpha$ MS/PSX Block Copolymers

A 2-liter, four-neck Morton flask was equipped with a mechanical stirrer, a thermometer and temperature controller, an addition funnel, a condenser, a nitrogen inlet, a means of distilling out solvent, and a viscometer for measuring the viscosity of the reaction solution. It is essential to exclude traces of water, which can react with the PSX oligomer end groups leading to altered stoichiometry and, therefore, low molecular weight products. The reactor was kept under a blanket of dry nitrogen throughout the reaction.

P $\alpha$ MS oligomer (40.0 g) and *o*-dichlorobenzene (1400 ml) were charged to the dried reactor. In order to remove all traces of water from the system, 600 ml of *o*-dichlorobenzene was distilled out. PSX oligomer (20,500  $M_n$ ) was added in increments over a period of two days at a reaction temperature of 180°C. During the first day, 82.8 g. was added in two equal portions. The reaction solution was allowed to stand at room temperature overnight. During the next day, three additional 10.0-g portions of PSX were added (total 112.8 g) at 2-hr intervals at 180°C. The reaction solution was again allowed to stand at room temperature overnight. Throughout the reaction, the viscosity of the solution increased, as measured by the viscometer, from an initial flow time of 14 sec to a final value of 423 sec. Evolution of dimethylamine was detected during the reaction by means of moist pH paper at the gas exit. On the third day, the product was isolated by precipitation with 10 volumes of methanol, reslurrying with methanol, and drying over night in vacuo at 80°C. The yield was 138.5 g (91.9%) of a white, rubbery crumb, reduced viscosity 0.71 (0.2 g/dl in  $\text{CH}_2\text{Cl}_2$  at 25°C). The properties of this copolymer are given in Table I (copolymer V).

The  $\bar{M}_n$  of the P $\alpha$ MS oligomer was calculated from the stoichiometry of the block copolymer reaction. A total of 112.8 g of PSX oligomer of 20,500  $\bar{M}_n$  was used, i.e., 0.0055 mole. Since high molecular weight block copolymer product was obtained, the 40.0 g of P $\alpha$ MS oligomer used also amounted to approximately 0.0055 mole. The  $\bar{M}_n$  of the P $\alpha$ MS oligomer was therefore  $40.00/0.0055 = 7273$  (7300 when rounded off).

Copolymers II-V were made by this procedure. Copolymer I was prepared in a similar manner, except that monochlorobenzene was used as the solvent and the reaction temperature was 120°C.

## DISCUSSION

### Synthesis

Poly( $\alpha$ -methylstyrene)-poly(dimethylsiloxane) (P $\alpha$ MS/PSX) block copolymers were prepared by the condensation of dihydroxyl-terminated

TABLE I  
Properties of Poly( $\alpha$ -methylstyrene)/Poly(dimethylsiloxane) Block Copolymers<sup>a</sup>

Copolymer ident.	Block $\bar{M}_n$ (P $\alpha$ MS/PSX) <sup>b</sup>	PSX, % wt-%	Reduced viscosity <sup>d</sup>	Tensile modulus, psi	Tensile strength, psi	Elongation at break, psi	$T_g$ , °C <sup>e</sup>	
							P $\alpha$ MS Block	PSX Block
I	2,900/5,200	64.4	0.33	13,000	700	550	+80	-120
II	7,300/1,700	20.7	0.59	235,000	4,500	2	+85	g
III	7,300/5,400	51.0	0.69	61,000	1,350	130	+130	g
IV	7,300/10,000	52.0	0.57	72,000	1,900	373	+140	g
V	7,300/20,500	73.2	0.71	5,000	1,300	935	+130	-105 and -45 <sup>f</sup>

<sup>a</sup> Mechanical properties measured on 10-mil films cast from chloroform solution, except copolymer IV, which was compression molded at 190°C.

<sup>b</sup>  $\bar{M}_n$  of PSX oligomers determined by potentiometric titration of amine endgroups.  $\bar{M}_n$  of P $\alpha$ MS oligomers calculated from stoichiometry of block copolymer synthesis reaction.

<sup>c</sup> Determined by NMR analysis or calculated from oligomer charge.

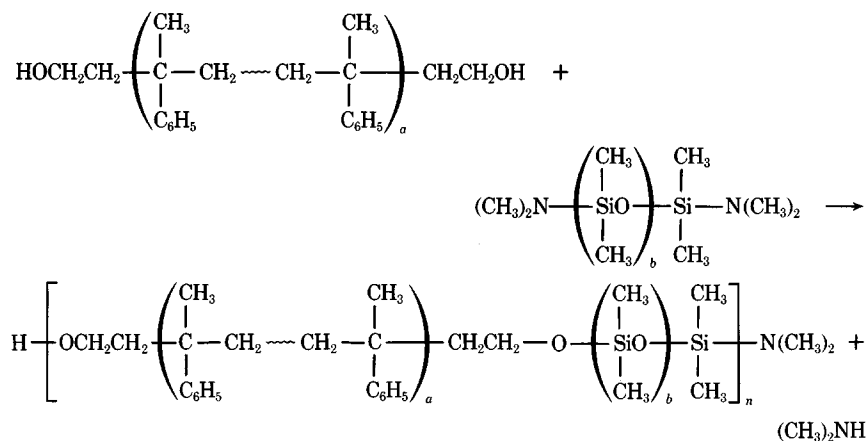
<sup>d</sup> Measured at 0.2 g/dl in methylene chloride at 25°C.

<sup>e</sup> Glass transition temperatures determined from modulus-temperature relationship.

<sup>f</sup> The -45°C transition is the crystalline melting point of the long PSX block.

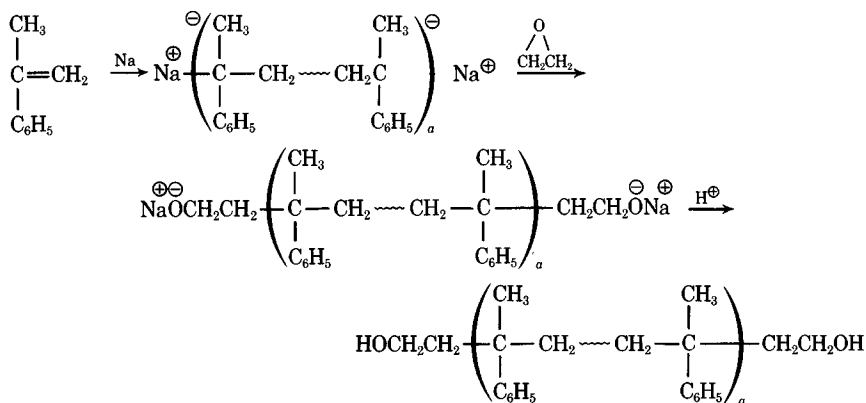
<sup>g</sup> Low-temperature  $T_g$  not measured.

P $\alpha$ MS oligomers with bisdimethylamino-terminated PSX oligomers, with the evolution of dimethylamine, as is shown in the following equation:



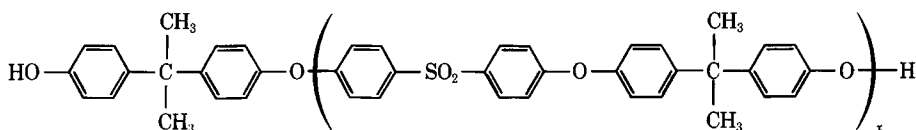
Obviously, the end blocks and endgroups of the copolymer will depend on the actual stoichiometry of the reaction, rather than as depicted above for the perfect 1/1 stoichiometry. The reactions were carried out either in chlorobenzene at 120°C or in *o*-dichlorobenzene at 180°C.

The P $\alpha$ MS oligomers were synthesized by nonaqueous dispersion polymerization of  $\alpha$ -methylstyrene anionically via initiation with sodium followed by "capping" with ethylene oxide and terminating with acetic acid:



The bisdimethylamino-terminated poly(dimethylsiloxane) oligomers used in this work were kindly supplied by Mr. T. Williams of the Silicones Department of Union Carbide Corporation.

The block copolymer synthesis reaction is similar to the one developed earlier for the synthesis of polysulfone-silicone block copolymers.<sup>15</sup> The latter reaction employs the same type of PSX oligomer, but the polysulfone oligomer,



bears phenolic hydroxyl endgroups in contrast to the aliphatic hydroxyl endgroups on the P $\alpha$ MS oligomers. As a result of this difference in end-group acidity, the P $\alpha$ MS oligomer reacts with the PSX oligomer at a much slower rate than does the polysulfone oligomer. This is in agreement with the literature,<sup>16,17,18</sup> which indicates that aliphatic alcohols react more slowly with aminosilanes than do phenols. A large difference in reactivity, which is illustrated in Figure 1, existed even when the temperature of the P $\alpha$ MS/PSX reaction was much higher than that of the polysulfone/PSX reaction (180°C vs. 70°C). However, in spite of the slow rate of reaction, it was possible to synthesize P $\alpha$ MS/PSX block copolymers of high molecular weight (see Table I) by incremental addition of the PSX oligomer to approach the stoichiometric endpoint gradually.

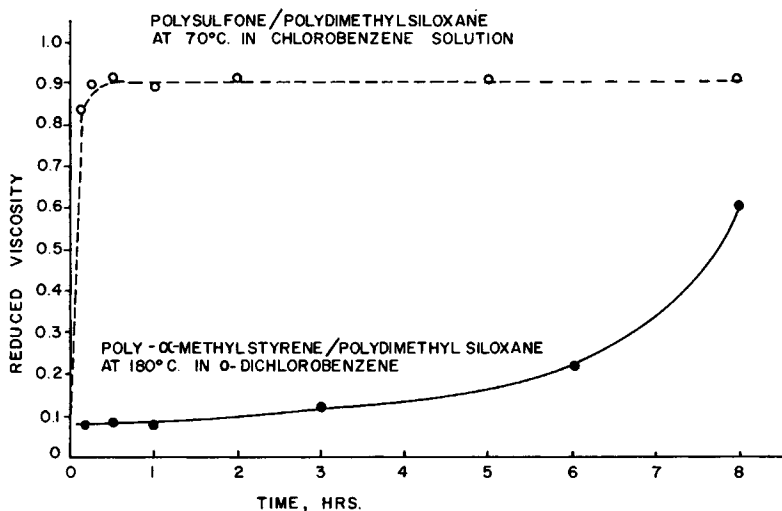


Fig. 1. Rate of block copolymer formation.

### Properties

Block copolymers were synthesized from oligomers of varying number-average molecular weight ( $\bar{M}_n$ ) to obtain products over a wide range of composition, i.e., wt % PSX. P $\alpha$ MS oligomers of 2,900 and 7,300  $\bar{M}_n$  and PSX oligomers ranging from 1,700 to 20,500  $\bar{M}_n$  were employed. All of the block copolymers produced strong, transparent films. The dependence of mechanical properties on copolymer composition is illustrated by the data in Table I. The products of greatest interest were copolymers I and V, which were high in PSX content (64.4% and 73.2%, respectively).

These block copolymers were elastomeric, low-modulus materials displaying high elongation and good recovery properties and could, therefore, be useful in thermoplastic elastomer applications. At the other end of the composition range, copolymer II was found to be a stiff, very brittle material (1 ft-lb/in.<sup>3</sup> pendulum impact strength), even though it contained 20.7% PSX. Copolymers III and IV were of intermediate composition and displayed intermediate properties. These two polymers were relatively tough, exhibiting pendulum impact strengths of 100 to 400 ft-lb/in.<sup>3</sup>

Block copolymers composed of segments which are basically incompatible with each other exist in separate microphases and display two-phase transition temperatures characteristic of each of the blocks.<sup>19</sup> Phase separation provides the physical "tie-down" points which give rise to the elastomeric properties of thermoplastic elastomer block copolymers, and these properties are displayed between the upper and lower phase transition temperatures.<sup>1,2</sup> The P $\alpha$ MS/PSX block copolymers are two-phase systems, as illustrated by the modulus/temperature relationships for copolymers I and V shown in Figure 2.

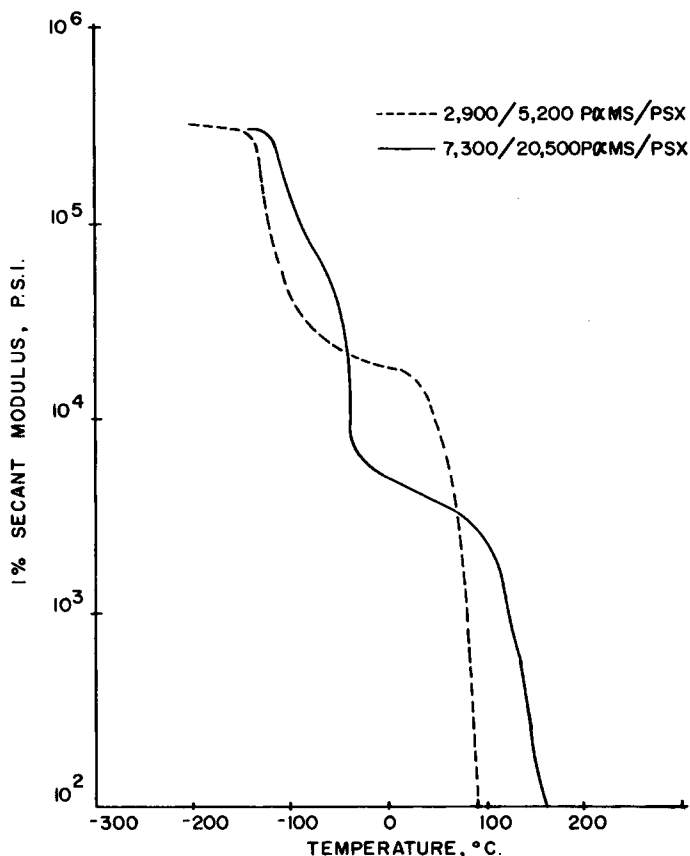


Fig. 2. Modulus-temperature relationship.

The glass transition temperatures ( $T_g$ ) of the P $\alpha$ MS and PSX blocks are reported in Table I. The  $T_g$  of the PSX blocks was fairly constant ( $-105^\circ\text{C}$  to  $-120^\circ\text{C}$ ) at block lengths of 5,200 and 20,500  $\bar{M}_n$ . However, the  $T_g$  of the P $\alpha$ MS blocks was dependent upon block molecular weight. At 2,900  $\bar{M}_n$  (copolymer I), the  $T_g$  was  $80^\circ\text{C}$ , but at 7,300  $\bar{M}_n$  (copolymers III, IV, and V), it was  $130^\circ$  to  $140^\circ\text{C}$ . The dependence of  $T_g$  on  $\bar{M}_n$  for  $\alpha$ -methylstyrene homopolymers has been reported by Cowie and Toporowski.<sup>4</sup> As is shown in Table II, their data agree quite well with the P $\alpha$ MS block  $T_g$  values obtained in our work. Their data also predict that block copolymers exhibiting a  $T_g$  in the vicinity of  $155^\circ\text{C}$  could be obtained by employing P $\alpha$ MS oligomers of about 20,000  $\bar{M}_n$ , which should be possible using our synthetic procedure. The low ( $85^\circ\text{C}$ )  $T_g$  of the 7,300  $\bar{M}_n$  P $\alpha$ MS block observed in copolymer II is believed to be due to a limited degree of phase blending of the P $\alpha$ MS block with the low (1,700) molecular weight PSX block, i.e., a "plasticizing" effect. It is interesting to note that copolymer V, which contains a 20,500  $\bar{M}_n$  PSX block, displayed a melting point transition at  $-45^\circ\text{C}$  characteristic of silicones, while copolymer I, with a shorter (5200  $\bar{M}_n$ ) PSX block, did not.

TABLE II  
 $T_g/\bar{M}_n$  Relationship for P $\alpha$ MS Blocks and Homopolymers

P $\alpha$ MS $\bar{M}_n$	P $\alpha$ MS $T_g$ , $^\circ\text{C}$	
	Block copolymer <sup>a</sup>	Homopolymer <sup>b</sup>
2,900	80	88
7,300	130-140	121
20,000	—	155
490,000	—	173 <sup>c</sup>

<sup>a</sup>  $T_g$  determined from modulus-temperature relationship.

<sup>b</sup> Data of Cowie and Toporowski;<sup>4</sup>  $T_g$  determined by differential thermal analysis.

<sup>c</sup> Asymptotic maximum  $T_g$ .

The P $\alpha$ MS/PSX block copolymers were found to display good compression moldability, as is demonstrated by the data in Table III. The properties of molded films of copolymers III and V were essentially equivalent to those of solution cast films (which should reflect ultimate properties).

## CONCLUSIONS

Block copolymers of poly( $\alpha$ -methylstyrene) and poly(dimethylsiloxane) have been synthesized by the condensation of dihydroxyl-terminated P $\alpha$ MS oligomers with bisdimethylamino-terminated PSX oligomers. The rate of reaction is slow, but a satisfactory procedure has been developed to prepare high molecular weight products. The copolymers have a repeating block sequence structure,  $\text{-(P}\alpha\text{MS/PSX)-}$ , and vary in properties as a function of composition. Low PSX-content ( $\sim 20\%$ ) copolymers are



TABLE III  
Properties of Molded and Solution-Cast Films

Copolymer ident.	Film fabrication <sup>a</sup>	Tensile modulus, psi	Tensile strength, psi	Elongation at break, %
III	molded <sup>b</sup>	65,000	1,250	60
	cast <sup>c</sup>	61,000	1,350	130
V	molded <sup>d</sup>	1,500	1,300	730
	cast <sup>c</sup>	5,000	1,300	930

<sup>a</sup> Ten-mil films.

<sup>b</sup> Compression molded at 230°C.

<sup>c</sup> Cast from chloroform solution.

<sup>d</sup> Compression molded at 190°C.

very brittle, intermediate compositions (~50% PSX) are tough, and high PSX-content (>65%) materials display elastomeric properties. As a result of dual glass transition temperatures at -120°C and +140°C (and possibly higher, if longer PαMS blocks are used), these block copolymers should have useful properties over a wide temperature range. In addition, the materials are compression moldable, and they are anticipated to have good stability.

### References

1. G. Holden, E. T. Bishop, and N. R. Legge, *J. Polym. Sci. C*, **26**, 37 (1969).
2. M. Morton, J. E. McGrath, and P. C. Juliano, *J. Polym. Sci. C*, **26**, 99 (1969).
3. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1966.
4. J. M. G. Cowie and P. M. Toporowski, *Eur. Polym. J.*, **4**, 621 (1968).
5. R. N. Meals and F. M. Lewis, *Silicones*, Reinhold, New York, 1959.
6. C. L. Lee and O. K. Johannson, *J. Polym. Sci. A-1*, **4**, 3013 (1966).
7. M. Morton and A. A. Rembaum, U.S. Pat. 3,051,684 (1962).
8. M. Morton, A. A. Rembaum, and E. E. Bostick, *J. Appl. Polym. Sci.*, **8**, 2707 (1964).
9. G. Greber, *Makromol. Chem.*, **101**, 104 (1967).
10. G. Greber, E. Reese, and A. Balciunas, *Farbe u. Lack*, **70**, 249 (1964).
11. G. Greber and A. Balciunas, *Makromol. Chem.*, **79**, 149 (1964).
12. Y. Minoura, M. Shundo, and Y. Enomoto, *J. Polym. Sci. A-1*, **6**, 979 (1968).
13. Y. Minoura, M. Shundo, and Y. Enomoto, *Kogyo Kagaku Zasshi*, **70**, 1025 (1967).
14. M. Mitoh, A. Tabuse, and Y. Minoura, *ibid.*, **70**, 1969 (1967).
15. A. Noshay, M. Matzner, and C. N. Merriam, *A.C.S. Polymer Preprints*, **12**, 247 (March 1971).
16. R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).
17. S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).
18. K. A. Andrianov, T. K. Dzahashiashvilli, V. V. Astakhin, and G. N. Shumakova, *Soviet Plast.*, 47 (Feb. 1968).
19. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
20. H. Brody, D. H. Richards, and M. Szwarc, *Chem. Ind. (London)*, 1473 (1958).
21. D. H. Richards, *J. Polym. Sci. B*, **6**, 417 (1968).
22. Y. Gallot and A. Marsiat, *C.R. Acad. Sci., Ser. C*, 272 (17), 1474 (1971).
23. E. E. Bostick, (General Electric). U.S. Pat. 3,483,270 (1969).

24. Y. Minoura, M. Mitoh, A. Tabuse, and Y. Yamada, *J. Polym. Sci. A-1*, **7**, 2753 (1969).
25. J. W. Dean, *J. Polym. Sci. B*, **8**, 677 (1970).
26. M. J. Owen and T. C. Kendrick, *Macromolecules*, **3**(4), 458 (1970).
27. J. C. Saam and F. W. G. Fearon; *Ind. Eng. Chem. Prod. Res. Develop.*, **10**, 10 (1971); *A.C.S. Polymer Preprints*, **11**(2), 455 (1970).
28. W. G. Davies and D. P. Jones, *Ind. Eng. Chem., Prod.*, **10**, 168 (1971); *A.C.S. Polymer Preprints*, **11**(2), 447 (1970).
29. G. B. Stampa, *J. Appl. Polym. Sci.*, **14**, 1227 (1970).
30. M. Narkis and A. V. Tobolski, *J. Macromol. Sci.-Phys.*, **B4**(4), 877 (1970).
31. H. A. Vaughn, *J. Polym. Sci. B*, **7**, 569 (1969).
32. R. P. Kambour, *J. Polym. Sci. B*, **7**, 573 (1969).
33. A. Noshay, M. Matzner, and C. N. Merriam, *J. Polym. Sci. A-1*, **9**, 3147 (1971).

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