Phase Continuity in Polystyrene–Nylon 6,10 Graft Copolymers

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Synopsis

Using a modified interfacial polymerization route, a graft copolymer of nylon 6,10 and polystyrene was prepared. First, an aqueous suspension of styrene monomer was encapsulated with nylon 6,10, followed by polymerization of the styrene to form the graft copolymer. When the material was subsequently molded below the crystalline melting point of nylon 6,10 (220°C), modulus–temperature behavior intermediate between polystyrene and nylon 6,10 was observed. However, when this graft copolymer was molded above the melting point of nylon 6,10, behavior more like pure polystyrene was observed. Phase contrast microscopy revealed that material molded below 220°C showed a continuous cellular-phase structure of about 30 microns in diameter, the interior of the cells being composed of polystyrene and the cell walls being composed of nylon 6,10. Phase inversion phenomenon was observed in the graft copolymer as the molding temperature was raised above 220°C. The nylon 6,10 phase became discontinuous, small globules being formed. This behavior is analogous to spheroidization in steel. It is thought that molten nylon 6,10 spheroidizes to attain a lower surface-energy state.

INTRODUCTION

Polymer blends, blocks, and grafts have achieved importance because they form two complementary phases, not in spite of it. In graft copolymers, phase morphology, particularly phase continuity, depends on the order of polymerization, mode of synthesis, and relative quantity of material.[1–10] In many known materials, the more continuous component exerts the dominant influence on the overall properties.

Both thermal and anionic techniques have been employed to graft polymerize nylon onto a polystyrene backbone.[11–18] Such polystyrene–nylon grafts offer an opportunity to intimately mix a tough, crystalline phase with a brittle, amorphous phase. However, the synthetic modes employed often favor greater phase continuity for the major component which is the brittle polystyrene. In the present paper, a synthetic mode which achieves phase continuity for the nylon component will be developed. By controlling the molding temperature of suspension-polymerized graft copolymers of polystyrene and nylon 6,10, it was found that phase continuity could be controlled.[19]
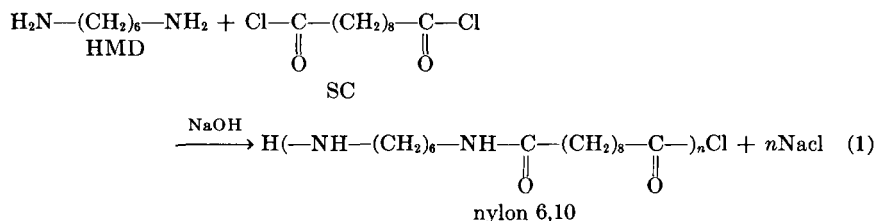
The materials discussed herein will be referred to as graft copolymers re-gardless of the extent of true chemical covalent bonds between the com-ponents, as this is conventional in modern nomenclature. Thus, the term graft copolymer, which can refer to either the chemically bonded materials or the general mode of synthesizing one polymer in the presence of the other, will be used more in the latter sense.

EXPERIMENTAL

Synthesis of Polystyrene–Nylon 6,10 Grafts

When the experimental work was begun, it was hoped that it would be possible to synthesize the polystyrene and nylon 6,10 simultaneously. However, simultaneous polymerization proved difficult, and the materials were synthesized more or less sequentially, nylon 6,10 being first.

Nylon 6,10 was polymerized by an adaptation of the well-known inter-facial polymerization technique[20] to suspension polymerization. When hexamethylenediamine (HMD) and sebacyl chloride (SC) are allowed to react, nylon 6,10 is obtained:

$$H_2N-(CH_2)_6-NH_2 + Cl-\underset{\underset{O}{\|}}{C}-(CH_2)_8-\underset{\underset{O}{\|}}{C}-Cl$$

$$\begin{array}{c} HMD \end{array} \qquad\qquad SC$$

$$\xrightarrow{\text{NaOH}} H(-NH-(CH_2)_6-NH-\underset{\underset{O}{\|}}{C}-(CH_2)_8-\underset{\underset{O}{\|}}{C}-)_nCl + n\text{Nacl} \quad (1)$$

$$\text{nylon 6,10}$$

As a general rule for interfacial polymerizations, it is desirable to use con-centrations of reactants such that 1 to 3 g polymer will be produced for every 100 ml combined water and organic solvent.[21] However, more con-centrated solutions were used in the following experiment.

The organic "solvent" used in the present synthesis was monomeric styrene. The synthesis was carried out in a three-neck flask. To prepare a 10% nylon 6,10 graft copolymer, the following proportions were used:

Solution I	Solution II	Solution III
water, 300 ml.	styrene, 100	water, 100 ml
poly(vinyl alcohol), 1 g	SC, 10 g	HMD, 4.9 g
	benzoyl peroxide, 1 g	NaOH, 3.36 g

All solutions were initially at room temperature. Figure 1 schematically illustrates the synthesis technique.

Initially, solution I is introduced in the flask. The poly(vinyl alcohol) in solution I behaves as a surfactant which keeps the oil phase dispersed. The flask is fitted with a stirrer, and solution I is stirred at moderately high speed. Solution III, containing HMD, is kept in an addition funnel and attached to one of the necks of the flask. N$_2$ is introduced in the flask for some time to remove the oxygen. Solution II is then rapidly added to the
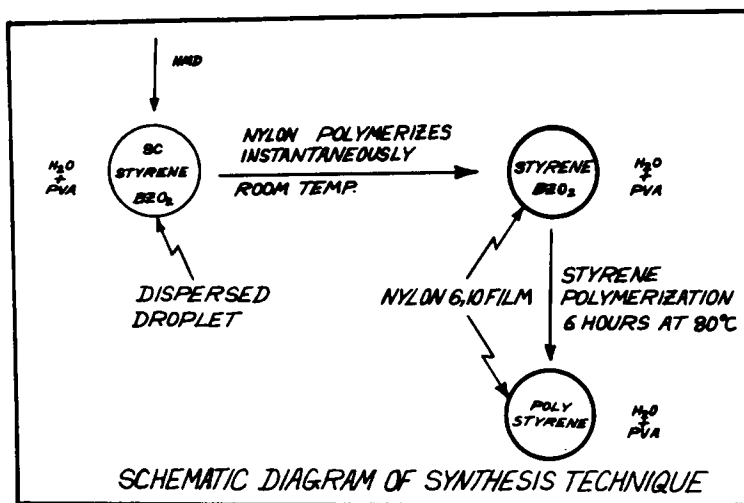
Fig. 1. Schematic diagram of the synthesis technique.

flask through the third neck. When solution II (oilphase) is uniformly dispersed, solution III from the addition funnel is quickly allowed to run into the flask. HMD immediately reacts with SC present in the droplets, and a nylon film is formed at the interface. In this way, each droplet of styrene monomer is encapsulated with nylon 6,10 film. The addition funnel is then removed and the flask is fitted with a thermometer and a reflux condensor. The temperature of the flask is then increased to 80°C and maintained at that temperature for 6 hr to ensure the complete polymerization of styrene.[22,23] After the reaction is over, the polymer is filtered out and washed thoroughly. The polymer is then dried at 50°C in a vacuum oven.

The dried suspension-sized polymer particles are then compression molded between aluminum foils at different temperatures through the range of 125–230°C for about 25 min, and under a pressure of 14 psig.

Discussion of the Synthetic Technique

The concentrations of HMD and SC used in the experiment are much higher than recommended.[21] Higher concentration of reactants gives a low molecular weight nylon. In the experiment described above, we could decrease the concentration of SC by either increasing the amount of styrene or introducing another organic solvent along with styrene. Let us examine each of these possibilities carefully. If the amount of styrene is increased to obtain the desired concentration of SC, then the percentage of nylon in the final polymer will be much too low. Secondly, if another organic solvent like carbon tetrachloride or xylene is introduced, then the final polymer will be plasticized and the morphology of the polymer may be different from what is anticipated. The high concentration of the reactants and concomitant low molecular weight nylon was accepted as the best alternative.

SC hydrolyses easily in the presence of water. The hydrolysis of the diacid chlorides is given by the following reaction equation:

$$R(COCl)_2 \xrightarrow{\text{H}_2\text{O}} R(COOH)_2 + 2HCl \qquad (2)$$
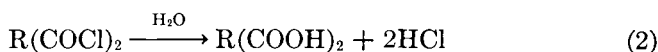
Wasley et al.[24] have shown that the hydrolysis of diacid chloride diminishes considerably with an increase in the molecular weight of these chlorides. The use of high molecular weight diacid chloride would still lead to the formation of a polyamide by interfacial polymerization.

To avoid extensive hydrolysis of SC, it is advisable to add HMD as soon as possible, precluding the simultaneous polymerization of styrene and nylon 6,10. (In an early attempt at simultaneous polymerization, solution II was dispersed in solution I, and the temperature was then raised to 80°C. Solution III, which contains HMD, was added very slowly so that the addition took about 3 hr. In this way, nylon 6,10 and styrene were presumably polymerized simultaneously. However, when the polymer formed in this manner was analyzed for its nitrogen content, surprisingly the sample had an abnormally low percentage of nitrogen, suggesting prior extensive hydrolysis of SC.)

In suspension polymerization, the particle size and size distribution are affected by the suspending agent and stirring rate. In the particle range of 10 to 1000 microns, Fondy and Bates[25] found that particle diameter varied inversely with impeller tip speed raised to the 1.8 power for a variety of impeller design. In our experiments, the particle size had a direct bearing on the size of the phase domain in the graft copolymer. However, in this work, no attempt was made to determine the size distribution of the suspension particles.

The possibility of a reaction between nylon 6,10 and poly(vinyl alcohol) does exist. Shimizu,[26] for example, has shown that polyamides could be modified with poly(vinyl alcohol) under certain conditions. While this possibility was not extensively investigated, the experimental results developed below suggest that any such reaction products were linear rather than crosslinked.

Instrumentation and Measurements

A Gehman Torsion Stiffness Tester[27,28] was used to measure the shear modulus, G, as a function of temperature. In this work the Young's modulus, E, is taken as three times the shear modulus G. The study was conducted from the room temperature to 180°C. Silicone oil was used as a bath fluid, with a rate of heating of about 1°C/min.

Since the grafts were synthesized by suspension polymerization, the size of the phase domains was expected to be of the order of several microns, therefore optical microscopy was expected to reveal the phase structure of these grafts. The samples were·cut to a thickness of about one to two microns with a Porter-Blum MT-2 ultramicrotome equipped with a diamond knife. Phase contract illumination[29] was found to be adequate to

produce the desired phase contrast between the two phases.   The phase structure was also studied by staining nylon phase with toluidine blue.[30]

RESULTS AND DISCUSSION

Modulus–Temperature Study

When these graft copolymers were compression molded, it was expected that they would mold only above 220°C, which is the crystalline melting point of nylon 6,10.   Surprisingly, it was found that these grafts could be molded at about 125°C, which is much lower than the melting point of nylon 6,10.   Figures 2 and 3 show the modulus–temperature behavior of these grafts when molded above and below the melting point of the nylon 6,10 component.

The results indicate a marked difference in behavior, depending on the molding temperature with respect to the melting point of nylon 6,10.   The grafts molded above the melting point of nylon 6,10 show polystyrene-like behavior, while grafts molded below the melting point of the nylon 6,10 show an average of nylon 6,10-like and polystyrene-like behavior.   Thus, it was established that the crystalline melting point of nylon 6,10 is the key
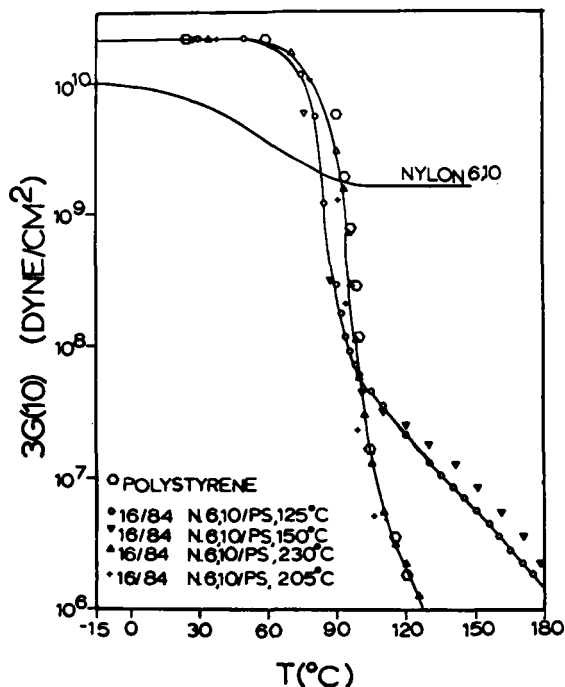

Fig. 2. Modulus–temperature behavior of 16/84 nylon 6,10/PS graft copolymers as a function of molding temperature.   Graft copolymers molded below the melting temperature of the nylon component have higher moduli above 100°C than expected. Data for nylon 6,10 homopolymer from ref. 34.
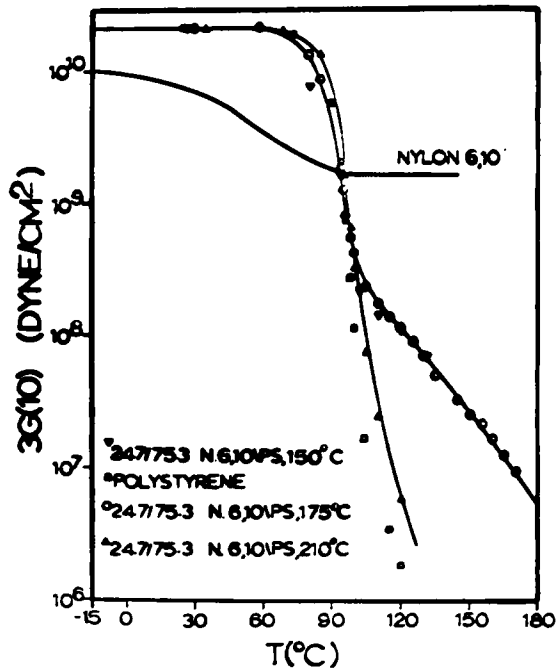
Fig. 3. Modulus–temperature behavior of 24.7/75.3 nylon 6,10/PS graft copolymers as a function of molding temperature.

variable in determining the properties of such grafts. It may be more proper to call the low-temperature molding operation a sintering phenomenon.[31]

Figure 4 illustrates how the modulus (measured at 120°C) of the graft copolymers changes with the molding temperature. The grafts molded below the melting point of nylon 6,10 have a significantly higher modulus at 120°C than that of the grafts molded above the melting point of nylon 6,10. The width of the transition zone in Figure 4 has been set arbitrarily. More experimental data are required to ascertain the exact width of the transition zone.

These results prompted us to examine the morphological change occurring in the graft copolymers due to high temperature molding.

Optical Microscopy

Because of the opacity or translucency, a multiple-phase structure was evident in the graft copolymers. The grafts were slightly yellowish in color. Two compositions of grafts, each molded above and below the melting point of nylon 6,10, were examined.

The most interesting result of this portion of the investigation was the distinct difference between the morphologies of the grafts molded below and above the melting point of nylon 6,10, as illustrated in Figures 5–7, which were obtained via phase contrast microscopy. The white area (Figs. 5–7)
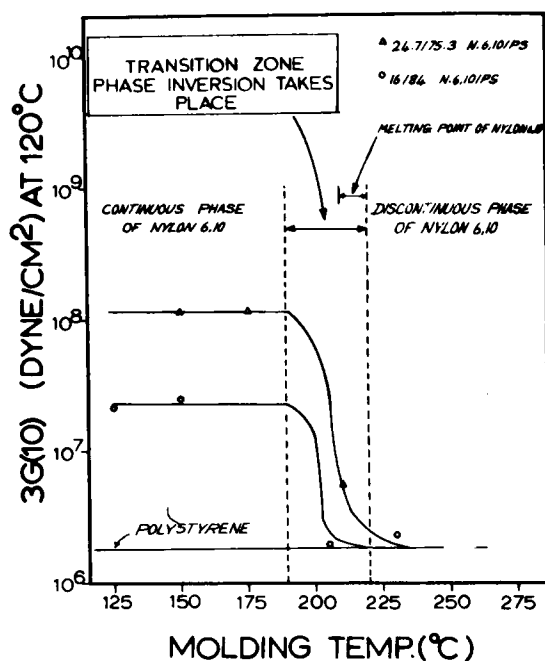
Fig. 4. Modulus at 120°C vs. molding temperature.

represents the nylon 6,10 phase, which was verified by staining the nylon 6,10 phase with toluidine blue[30] (Fig. 8).

Grafts molded below the melting point of nylon 6,10 show a continuous-phase structure of nylon 6,10.   The size of the polystyrene phase domains
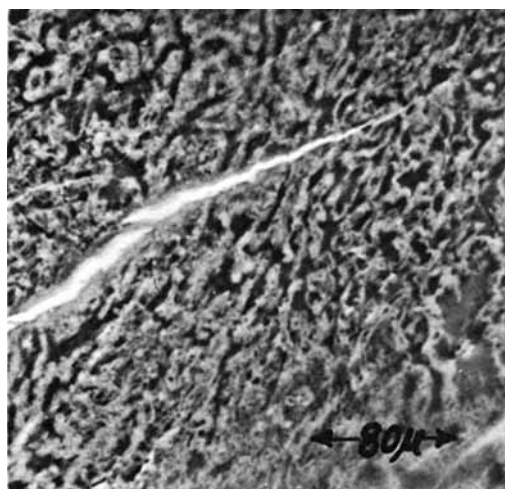

Fig. 5. Optical micrograph of 16/84 nylon 6,10/PS graft copolymer molded at 125° C via phase contrast microscopy.   A cellular structure is seen.   The cell walls (white area) are made of nylon 6,10 component, and the interior of the cells (dark area) is composed of polystyrene phase.
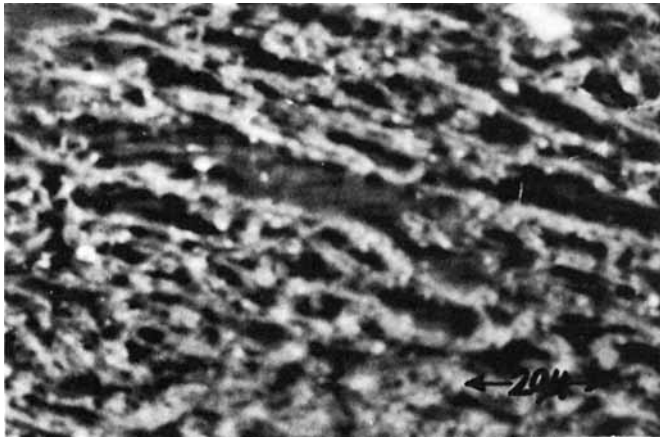
Fig. 6. Optical micrograph of 16/84 nylon 6,10/PS graft copolymer molded at 150°C. The cellular structure still exists.   The white cell walls, which represent nylon 6,10 phase, are not completely homogeneous.   Dark dots in the white area represent the presence of a finely dispersed polystyrene phase.

is about 10–30 microns, which represents the expected size of the suspension particles.   The nylon 6,10 film surrounding the polystyrene-phase domains is not completely homogeneous, however, as shown in Figure 6. There are small islands of polystyrene scattered throughout the nylon 6,10 film.   During synthesis when nylon film is formed, it is highly swollen with
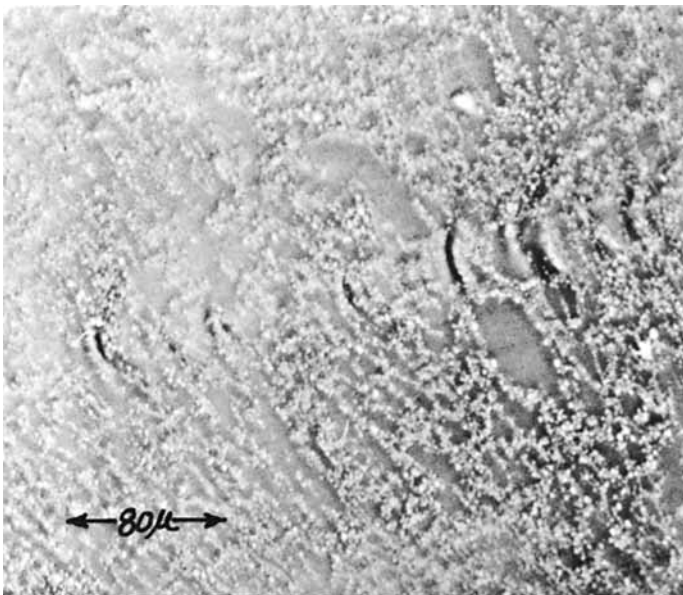

Fig. 7. Optical micrograph of 16/84 nylon 6,10/PS graft copolymer molded at 230°C. Cellular structure has been destroyed and phase inversion has taken place.   Nylon 6,10 component (white dots) has formed into small globules, and polystyrene (dark area) has become the continuous phase.
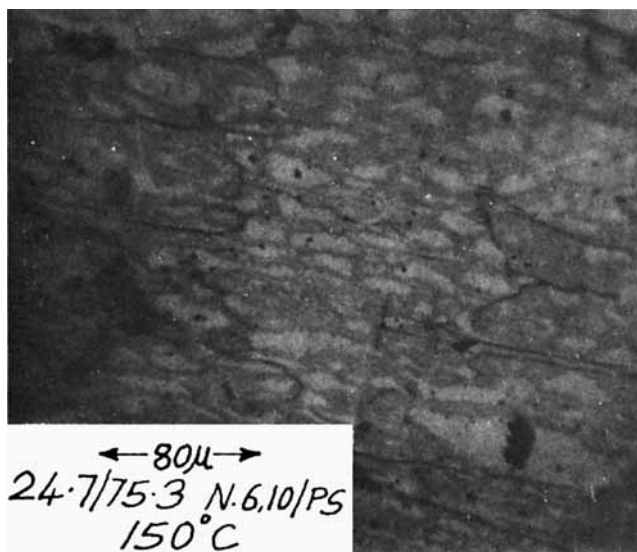
Fig. 8. Optical micrograph of 24.7/75.3 nylon 6,10/PS graft copolymer molded at 150°C. The nylon 6,10 phase has been stained with toluidine blue.[30] The phase structure seen here confirms the phase structure observed by the phase contrast microscopy.

styrene monomer. As polymerization proceeds, islands of polystyrene are formed within the film by subsequent phase separation. This structure is thought to help in molding such grafts below the melting point of nylon 6,10. When the same graft copolymer is molded above the nylon 6,10 melting point, phase inversion occurs. The nylon 6,10 becomes the discontinuous phase, while polystyrene becomes the continuous phase, as illustrated in Figure 7. The continuous-phase structure of polystyrene is then responsible for the polystyrene-like behavior upon molding above 220°C.

This behavior is analogous to spheroidization in steel.[32,33] Minimum hardness and maximum ductility of steel can be produced by a process called spheroidizing, which causes the iron carbide to form in small spheres or nodules in a ferrite matrix. In pearlite, the carbide is lamellar. However, if the pearlite steel were held just under the eutectoid temperature for prolonged periods of time, the carbide spheroidizes to form its more stable and lower surface-energy state of small rounded globules. Similarly, in this graft copolymer, when it is molded above the melting point of nylon 6,10, nylon presumably spheroidizes to attain the lower surface-energy state.

CONCLUSIONS

The novel synthesis technique discussed herein forms a continuous-phase structure of nylon and a discontinuous phase of polystyrene, although the former is the minor component in the graft copolymer by weight.

The mechanical properties of these graft copolymers were found to depend on the phase structure and nylon concentration. The continuous-

phase structure of nylon 6,10 significantly improves the high-temperature modulus of these grafts, as shown in Figure 4. Conventional blending technique would have favored a discontinuous-phase structure for nylon 6,10, since it was the minor phase. The grafts having discontinuous-phase structure of nylon have poorer high-temperature mechanical properties than those of grafts having continuous-phase structure of nylon. Increasing the nylon concentration results in better mechanical properties of these graft copolymers (Fig. 4).

References

1. K. Kato, *Jap. Plast.*, **2**, 6 (April 1968).
2. M. Matsuo, *Jap. Plast.*, **2**, 6 (July 1968).
3. M. Szwarc, *Polym. Eng. Sci.*, **13**, 1 (1973).
4. M. Shen and M. V. Bever, *J. Mater. Sci.*, **7**, 741 (1972).
5. G. E. Molau, Ed., *Colloidal and Morphological Behavior of Block and Graft Copolymers*, Plenum Press, New York, 1971.
6. H. Keskkula, Ed., *Polymer Modification of Rubbers and Plastics*, Interscience, New York, 1968.
7. S. L. Aggarwal, Ed., *Block Polymers*, Plenum Press, New York, 1970.
8. H. Battaerd and G. Tregear, *Graft Copolymers*, Interscience, New York, 1967.
9. W. J. Burlant and A. S. Hoffman, *Block and Graft Polymers*, Reinhold, New York, 1960.
10. Volker Huelck, D. A. Thomas, and L. H. Sperling, *Macromolecules*, **5**, 340, 348 (1972).
11. P. J. Flory (assigned to Wingfoot Corp. Akron, Ohio), U.S. Pat. 2,524,045, October 3, 1950.
12. C. B. Chapman and L. Valentine, *J. Polym. Sci.*, **34**, 319 (1959).
13. D. Lim and H. Morawetz, *J. Colloid Sci.*, **20**, 241 (1965).
14. O. Wichterle and V. Grego, *J. Polym. Sci.*, **34**, 309 (1959).
15. R. M. Hedrick, E. H. Mottus, and J. M. Butler, U.S. Pat. 3,136,738 (1965).
16. V. V. Korshak, A. A. Silin, T. M. Frunze, I. V. Krgel'skii, E. A. Dukhooskii, and E. L. Baranov, *Mekh. Polim.*, **4**, 559 (1968).
17. M. Matzner, D. L. Schober, and J. E. McGrath, *Polym. Preprints*, **13** (2), 754 (1972); *Eur. Polym. J.*, **9**, 469 (1973).
18. R. A. Cooper, Ph.D. Dissertation, Polytechnical Institute of Brooklyn, 1971.
19. J. Khandheria, M.S. Thesis, Lehigh University, 1973.
20. P. W. Morgan, *Condensation Polymers: by Interfacial and Solution Methods*, Interscience, New York, 1965.
21. R. G. Beaman, P. W. Morgan, C. R. Koller, E. L. Wittbecker, and E. E. Magat, *J. Polym. Sci.*, **40**, 329 (1959).
22. E. M. McCaffery, *Laboratory Preparation for Macromolecular Chemistry*, McGraw-Hill, New York, 1970, p. 85.
23. *Polymer Processes: Chemical Technology of Plastics, Resins, rubbers, adhesives, and fibres*, Vol. X, C. E. Schildknecht, Ed., Interscience, New York (1956).
24. W. L. Wasley, R. E. Whitfield, L. A. Miller, and R. Y. Kodani, *Text. Res. J.*, **33**, 1029 (1963).
25. P. L. Fondy and R. L. Bates, *A.I.Ch.E. J.*, **9**, 338 (1963).

26. A. Shimizu, *Chem. Abstr.*, **70**, 78907p (1969).

27. ASTM D1052-58T, American Society for Testing Materials, Philadelphia, 1958.

28. S. D. Gehman, D. E. Woodford, and C. S. Wilkinson, Jr., *Ind. Eng. Chem.*, **39**, 1108 (1947).

29. J. H. Richardson, *Optical Microscopy for the Materials*, Marcel Dekker, New York, 1971.

30. J. R. Baker, *Principles of Biological Microtechnique*, Wiley, New York, 1958.

31. G. R. Steiner, C. Nippert, and J. A. Manson, *Polym. Preprints*, **11** (2), 1168 (1970).

32. H. D. Moore and D. R. Kibbey, *Manufacturing Materials and Processes*, R. D. Irwin, Homewood, Illinois, 1965.

33. L. H. Van Vlack, *Elements of Materials Science; An Introductory Text for Engineering Students*, 2nd ed., Addison Wesley, Reading, Mass., (1964).

34. *Encyclopedia of Polymer Science and Technology*, Vol. 10, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Interscience, New York, 1968, p. 469.