Polyester–Polycarbonate Blends. I.
Poly(butylene Terephthalate)

D. C. WAHRMUND,* D. R. PAUL, and J. W. BARLOW, *Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712*

Synopsis

Melt blends of bisphenol A polycarbonate with poly(butylene terephthalate) were studied by DTA and dynamic mechanical behavior to determine their state of miscibility. Both techniques showed multiple glass transitions indicative of incomplete miscibility in the amorphous phase. However, these transitions in some cases did not correspond to those in the pure components and varied with overall blend composition in some instances. This indicates that there are amorphous phases containing both components, i.e., partial miscibility. This view was supported by the crystallization behavior of the polyester. Two crystallization exotherms were observed for quenched samples, which is interpreted as polyester crystallization from two separate phases, one richer in this component than the other. Other interpretations of these results are discussed.

INTRODUCTION

Recently, it has been observed[1] that a number of polyesters show varying degrees of partial miscibility or total miscibility with the polycarbonate based on bisphenol A. This behavior is quite interesting because of the potential applications of such blends. In this series of papers, the detailed results from a continuing investigation of polyester–polycarbonate blends is presented. The main purpose is to use transitional and crystallization behavior to gain insight into the state of miscibility of these systems and how this is affected by the chemical structure of the polyester.

This paper deals with the relatively new engineering thermoplastic poly(butylene terephthalate) (PBT). A brief scan of the trade and patent literature suggests that there is considerable commercial interest in blends of PBT with polycarbonate (PC)[2-7]; however, there appear to be no reports of a fundamental nature about these blends. As shown here, PC–PBT blends are certainly not totally miscible, although there is a definite degree of partial miscibility which may serve some useful purposes. Later papers will give results for other polyesters that exhibit a greater degree of miscibility, including complete miscibility, with PC.

* Present address: Exxon Chemicals USA, Baton Rouge, Louisiana 70821.

EXPERIMENTAL

Both polymers used in this study were commercial products supplied by the General Electric Company. The PC was Lexan 310 while the PBT was Valox 310. Both polymers were dried at 120°C for 2 hr prior to melt processing in order to avoid degradation by water.

Melt blending was done in a Brabender Plasticorder at 250°C for 10 min. By this time the torque had stabilized. In certain cases the polymers were slightly discolored. This processing temperature was selected because it is above the 232°C melting point of PBT. While the melting point of PC is reported to be 267°C, this polymer was never observed to crystallize in this study.

During melt mixing, pure PC and PBT were quite transparent, as were blends containing 10% and 75% by weight of PBT. The adjacent compositions, 20% and 50% PBT, had a satiny appearance and were opaque. Blends between these limits, containing 30% and 40% PBT, were light brown in color and were translucent to opaque in clarity.

After mixing was completed, the melt was transferred to a compression mold preset at 250°C where a $\frac{1}{8}$-in. sheet was formed and subsequently cooled to room temperature. Sheets containing more than 30% PBT were opaque. The 30% PBT sheet ranked between translucent to opaque. The 20% PBT sheet was virtually transparent though somewhat hazy. The 10% PBT sheet was as transparent as the pure PC sheet. Interestingly, however, small specimens of every composition, except pure PBT, were clear after quenching into liquid nitrogen from the melt. These samples remained clear for the several months they were observed.

DTA RESULTS

Blends prepared by the procedures described above were examined by differential thermal analysis in order to establish their glass transition, melting, and crystallization behavior. For many of these observations, cyclic heating at 10°C/min to 250°C and cooling at 20°C/min to −120°C was used. In these cases, the identical results obtained on all heats after the first are of interest. However, for selected quenched or annealed samples only the first heat is of interest.

The upper eight thermograms of Figure 1 are typical representations of cyclic heating experiments for various compositions in this system. The pure PC showed a T_g at 145°C and no evidence of melting even when heated to higher temperatures. The pure PBT showed a T_g at 36°C and a T_m of 232.5°C using the cyclic heating and cooling schedule. The location of the T_m and its shape varied with prior history, but cyclic heating gave rather reproducible values. Frequently, first heats showed a crystallization exotherm, although for pure PBT none was observed on subsequent cyclic heatings.

All blends showed evidence of PBT melting. The location of this melting endotherm remained nearly the same as that of pure PBT until about 50% PC was added. The lower part of Figure 2 shows that further PC addition results in a slight lowering of the PBT melting point; however, at 90% PC this reduction is only 4.5°C. Each point shown there is the average of four to 12 observations, with the range of deviations being typically ±2°C from the average.

The area of this endotherm peak, in arbitrary units adjusted for sample size, is shown in the upper part of Figure 2. These data lie near the straight line
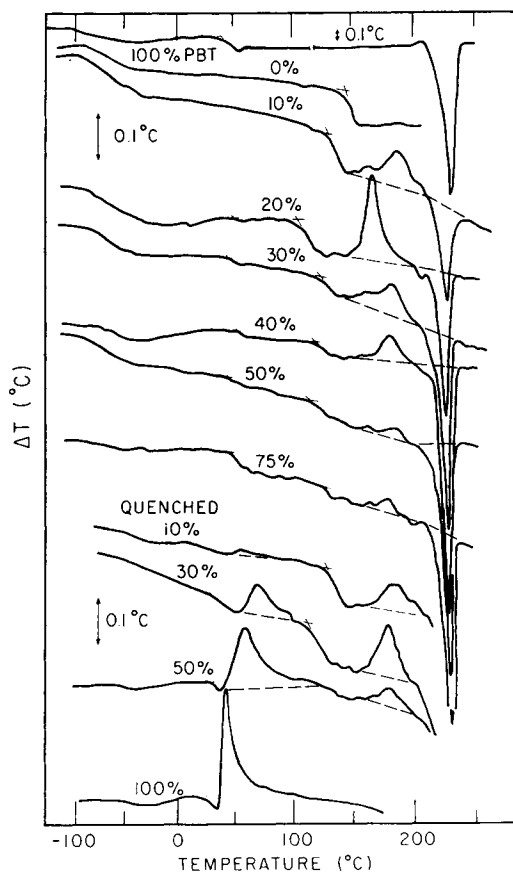
Fig. 1. DTA thermograms for various PC–PBT blends at heating rate of 10°C/min. Upper curves obtained after cooling at 20°C/min, while lower ones used samples quenched from the melt into liquid nitrogen.

connecting the extreme points. There seems to be a trend in the departures from this line, but no reason for this can be offered if, in fact, this trend is significant. Observations about the kinetics of crystallization from these blends will be discussed later.

Certain glass transition features of these blends are evident from the thermograms shown in Figure 1; however, separate thermograms run on a more sensitive scale prior to melting form the basis for the following discussion. All blends showed some evidence for at least two glass transitions. Blends containing only 10% and 20% PBT showed very distinct glass transitions similar to that of pure PC, except that these were lower by 17° and 36°C, respectively. These transitions might intersect with the $T_g = 36°C$ of PBT if this trend with composition were continued (see upper part of Fig. 3). However, a similar transition for the 30% PBT was observed at the higher temperature of 125°C. Blends with higher PBT content showed a similar transition at about the same temperature (upper curve in top part of Fig. 3) which decreased in magnitude with increasing PBT content as shown in the bottom part of Figure 3.

The 75% PBT blend showed a very distinct transition similar to the PBT T_g, only shifted upward by 13°C. This transition falls on the central curve in the
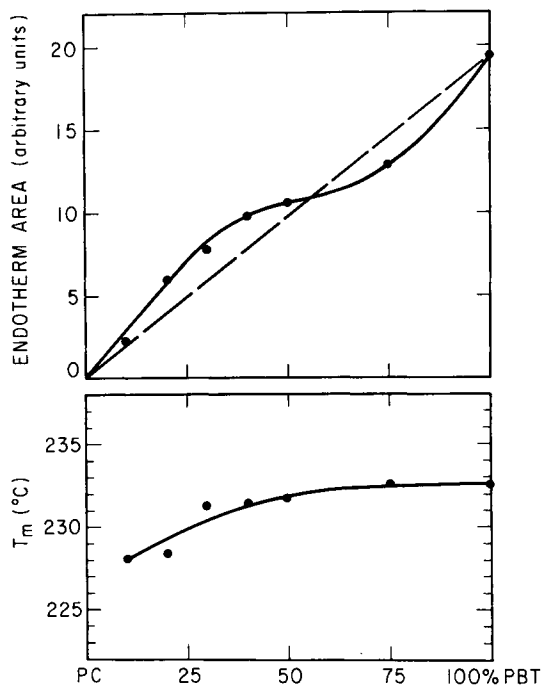
Fig. 2. Melting behavior of PC–PBT blends on cyclic heating.

top part of Figure 3 which connects simply with the similarly distinct transitions for the 10% and 20% PBT blends. Blends containing less PBT exhibited transitions at a similar temperature which decreased in intensity as the PBT content decreased. The lower curve in the top part of Figure 3 shows the temperature at which this transition occurred. The magnitudes of all transitions are shown in the lower part of Figure 3, using symbols that key them to their temperature locations given in the top part of this figure. Evidently, every blend contains at least two amorphous phases. However, since their T_g's do not correspond to pure PBT or PC as shown in Figure 3, these phases are evidently mixtures of the two polymers.

In addition to these two amorphous phases, there is a crystalline phase of presumably pure PBT. The kinetic characteristics of PBT crystallization from these belnds provide some additional information in support of the partial miscibility picture indicated above. First, it is interesting to note that each blend shows a crystallization exotherm on heating at 10°C/min after cooling at 20°C/min (see upper thermograms in Fig. 1). Pure PBT does not show this. Evidently, PBT crystallizes more slowly from the blends as would be expected from a mixed amorphous phase. Because of this delay in crystallization, the amount of crystallinity in the region of the observed T_g's is less than that indicated in Figure 2. This fact complicates any conclusions about the amount of the amorphous phases that might be inferred from the magnitudes of the various T_g's shown in Figure 3.

First heats of blends quenched from the melt into liquid nitrogen shown in the lower part of Figure 1 also show some interesting insights into the crystallization process. Pure PBT when so quenched shows a crystallization exotherm on heating immediately following its T_g. Each blend, however, shows two
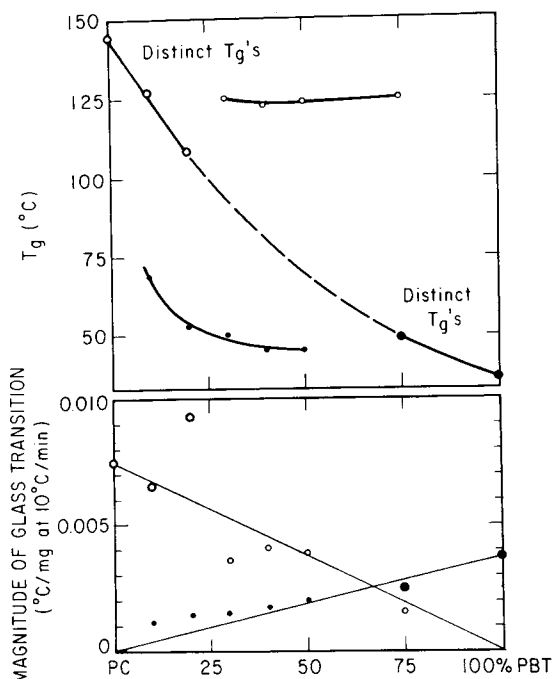
Fig. 3. Glass transitions and their magnitudes observed during cyclic heating of PC–PBT blends. Symbols key magnitudes and temperature locations.

crystallization exotherms (see Fig. 1). The first occurs following the lower T_g and apparently represents PBT crystallizing from a PBT-rich phase. The second occurs after the higher T_g and evidently represents PBT crystallizing from a PC-rich phase.

During the cycled DTA runs, only one exotherm was observed. Evidently, the crystallization from the PBT-rich phase was able to occur during the slower, 20°C/min, cooling. In these cases, the average ratios of the single exotherm area to the endotherm area were 0.84 for the 10% PBT blend and 0.90 for the 20% PBT blend, dropped to 0.33 for the 30% blend, and gradually decreased to zero as PBT content increased further.

Annealing at 175°C for 10 min allowed maximum crystallinity to develop in a 20% PBT blend. A subsequent thermogram showed no crystallization peak at all. The higher T_g was shifted upward to almost that of pure PC and was reduced in magnitude to about 90% of that for PC. Evidently, the amount and composition of each of the two amorphous phases are strong functions of prior thermal history.

RESULTS FROM DYNAMIC MECHANICAL TESTING

Thin films pressed from the sheets described earlier were used to obtain dynamic mechanical properties at 110 Hz via a Rheovibron. These samples were annealed at 120°C for 30 min. This was done to ensure a uniform thermal history and to prevent crystallization from occurring during testing which would obscure the results. Thus, these results are not expected to be directly related to the DTA findings because this procedure alters the phase compositions as described earlier. The nature of the two techniques makes this unavoidable.

Pure Components

Figures 4 and 5 show plots of E', E'', and tan δ versus temperature for pure PC, pure PBT, and selected blends obtained here. For each of the pure polymers there are two prominent peaks or relaxations in the range of temperature shown. For polycarbonate, the highest temperature peak corresponds to the glass transition and is found at approximately 150°C on the E'' curve and at 158°C on the tan δ curve. Above 150°C, the tan δ readings were beyond the range of the Rheovibron; however, it was possible to follow these values qualitatively (see dashed lines) in order to locate the peak positions on the temperature scale. A lower temperature peak appears at −70°C on both the tan δ and E'' curves for PC.

The relaxations of PC have been reported on extensively.[8–12] The locations of these processes on the temperature scale described above agree well with the observations of others when compared at the 110 Hz used here. In one interpretation, the lower temperature relaxation at −70°C has been attributed to motions of the carbonate group[12]; however, others[8] have questioned this simple picture.

The PBT sample shows a high temperature relaxation at 60°C on the E'' curve and at 70°C in terms of tan δ. A low-temperature relaxation occurs at −70°C on the E'' curve and at −67°C on the tan δ curve. The relaxation behavior of various poly(methylene terephthalates) has been the subject of numerous investigations[8,13–20]; however, poly(ethylene terephthalate) is the most widely studied member of this homologous series. For poly(butylene terephthalate), the higher temperature relaxation is the result of the glass transition. Evidently, its location may be affected by the level and nature of the crystallinity[19] and
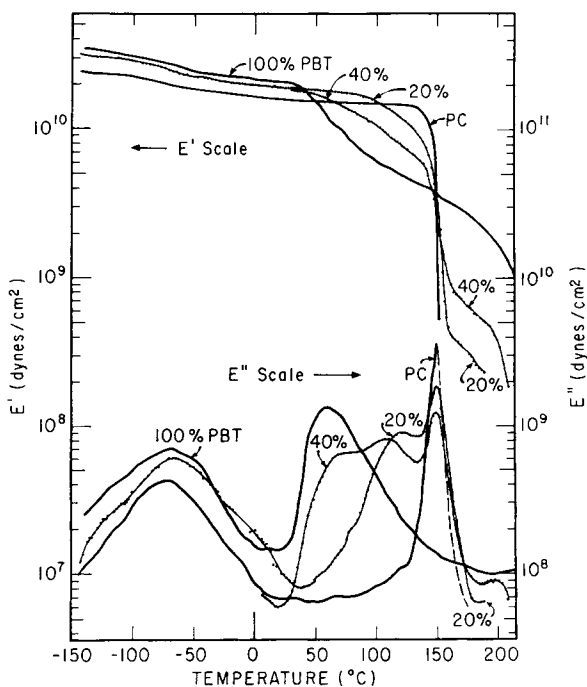

Fig. 4. Rheovibron storage and loss moduli at 110 Hz for PC, PBT and selected blends obtained on annealed samples. Some blend results omitted for clarity.
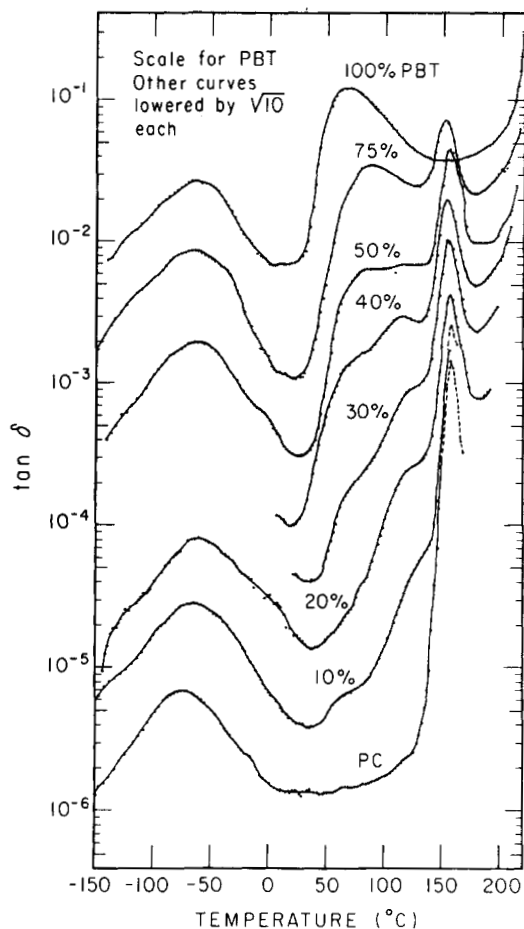
Fig. 5. Tan δ curves (shifted for visual display) corresponding to moduli data in Figure 5. All blend data are shown here.

perhaps molecular orientation, as is well established for poly(ethylene terephthalate). The lower temperature relaxation apparently arises from motions of various chemical groups in the chain and may be the result of several overlapping processes. The locations of these peaks on the temperature scale reported here agree rather well with those observed by others.

There is evidence that sorbed water affects the location of the relaxations of polyesters.[16] However, the annealing procedures used here should have eliminated most of this water from the present samples so that this should not be a factor.

Blends

The low-temperature peaks for PBT and PC are similar in shape and location. Thus, it is not surprising to see in Figures 4 and 5 that each blend shows a similar relaxation whose temperature location is essentially independent of PBT content.

However, the higher-temperature peaks for the blends show interesting trends

that approximately parallel the results from DTA measurements. Each blend shows a peak similar to the glass transition of PC, indicating the presence of an essentially pure polycarbonate phase. The magnitude of this peak steadily decreases as the PBT content increases but occurs at about the same temperature as in pure PC (see solid points in Fig. 6). Blends rich in PBT show a peak similar to the high-temperature transition of PBT but about 15°C or so higher. As the PBT content is lowered, this peak rapidly becomes smaller and is only a shoulder at 40% PBT. For blends more dilute in PBT, there is only a faint bump in this region. The open circles in Figure 6 show the approximate location of this transition for each blend. Its elevation in temperature, compared to PBT, suggests that it results from an amorphous phase rich in PBT with a nearly constant amount of PC when the total PBT content is below 75%.

A very intriguing feature of these data is a new peak intermediate between the two described above. It does not seem to be present in the 75% PBT blend, but at lower levels it is plainly evident (see especially the 40% PBT curves for E'' and tan δ in Figs. 4 and 5). The approximate location of this new peak is shown by the open squares in Figure 6 as a function of the total PBT content of the blend. Evidently, this peak is indicative of an amorphous phase containing both PC and PBT in proportions that depend on overall blend composition.

The lines shown in Figure 6 have been drawn to suggest how these various transitions might be related. On this basis, there would appear to be three amorphous phases in these samples at least in the middle of the composition range. One appears to be rather pure PC. Another seems to contain a constant but high proportion of PBT. The third contains both polymers in proportions more or less similar to the overall blend composition. At either extremity there may be only two phases; however, this apparent result may stem from an inability to resolve three peaks.

Although this picture qualitatively parallels that developed from the DTA results (compare Figs. 3 and 6), the two are not identical in detail. Because of the different thermal treatments, the phase compositions and proportions actually tested by the two techniques are probably different as discussed previously. It is quite probable that neither reflects an equilibrium situation. However, both conclusively show that there are multiple amorphous phases in this system some of which contain presumably homogeneous mixtures of the two polymers.
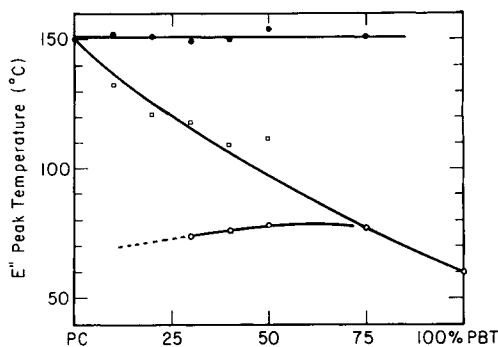

Fig. 6. Location of various relaxation peaks for annealed PC–PBT blends.

SUMMARY

Amorphous blends of miscible polymers are expected to show a single T_g, dependent on composition, located intermediate between the T_g's of the pure components.[21] If one of the components is crystallizable, a portion of this component will usually form a separate, purely crystalline phase when thermodynamic and kinetic conditions permit.[22–24] Thus, the T_g behavior should reflect the state of mixing in the remaining amorphous phase, and ideally the melting point of the crystalline phase will be depressed by its equilibrium with this phase.[23,24] The observations reported here for blends of poly(butylene terephthalate) with polycarbonate suggest that this system shows more than one amorphous phase containing essentially pure components in some cases but mixed phases in the other. This conclusion is based primarily on the location of multiple glass transitions some of which do not correspond to either pure polymer and depend on overall blend composition in some instances. This view is supported by observations of the crystallization behavior of PBT using simple hypotheses. The PBT melting point is slightly depressed for blends rich in PC. However, this fact cannot be easily interpreted as a classical depression by a diluent because of the sensitivity of the pure PBT melting point to various factors and the complex number and nature of any amorphous phases with which crystalline PBT might be in equilibrium.

It would be interesting to develop a complete phase diagram to describe this picture of partial miscibility of the amorphouse phase; however, this has not been possible from the present results. One might use simple assumptions to make rough quantitative estimates of the composition of the amorphous phases based on the glass transitions they exhibit. However, in the present case the compositions of these phases deduced in such a manner changed considerably with previous thermal history. Very likely, true equilibrium between these phases was not established. One might speculate that either upper or lower critical solution temperatures exist in this system. If they do, their presence has been obscured in the present study by their relation on the temperature scale to the melting point and glass transitions.

Other interpretations of the present observations may be possible. Certainly, one theoretical possibility is that chemical reactions may occur between a polycarbonate and a polyester during high-temperature melt processing. For example, one might propose that some type of interchange reaction occurs which in the extreme case would result in a random copolymer that shows a single T_g depending smoothly on blend composition. In less extreme cases, such a reaction might not go to completion but would produce multiple phases with intermediate glass transitions or procduce blocklike copolymers. Any extensive chemical reaction of this type would certainly make a dramatic reduction in the observed melting point or produce multiple melting points. This was not observed here. Subsequent papers in this series will address such chemical possibilities in greater detail. At the present time there is no evidence for any substantial effect of such reactions, and the presently offered explanation in terms of partial miscibility is preferred.

References

1. D. R. Paul, J. W. Barlow, C. A. Cruz, R. N. Mohn, T. R. Nassar, and D. C. Wahrmund, *Am. Chem. Soc. Org. Coat. Plast. Div. Prepr.,* **37** (1), 130 (1977).
2. Anon., *Chem. Eng. News,* **April 5,** 14 (1976).
3. T. Kaneko and M. Takamatsu (to Teijin), Jpn. Pat. 115,146 (1974); *Chem. Abstr.,* **82,** 99,299 (1975).
4. M. Matsukane and C. Azo (to Teijin), Jpn. Pat. 54,160 (1973); *Chem. Abstr.* **82,** 58,832 (1975).
5. J. Yamamoto, M. Ueno, and K. Umeda (to Teijin), Jpn. Pat. 80,162 (1974); *Chem. Abstr.,* **82,** 59,321 (1975).
6. A. D. Wambach (to General Electric), Ger. Pat. 2,310,742 (1973); *Chem. Abstr.,* **80,** 84,186 (1974).
7. Y. Nakamura, R. Hasegawa, and H. Kubota (to Teijin), Ger. Pat. 2,343,609 (1974); *Chem. Abstr.,* **81,** 64,626 (1974).
8. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* Wiley, London, 1967.
9. G. P. Mikhailov and M. P. Eidelnant, *Vysokomol. Soedin.,* **2,** 287 (1960).
10. Y. Ishida and S. Matsuoka, *Am. Chem. Soc. Polym. Div. Prepr.,* **6** (2), 795 (1965).
11. K. H. Illers and H. Breuer, *Kolloid Z.,* **176,** 110 (1961).
12. F. P. Reding, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.,* **54,** 556 (1961).
13. K. H. Illers and H. Breuer, *J. Colloid Sci.,* **18,** 1 (1963).
14. G. Farrow, J. McIntosh, and I. M. Ward, *Makromol. Chem.,* **38,** 147 (1960).
15. I. M. Ward, *Trans. Faraday Soc.,* **56,** 648 (1960).
16. W. Reddish, *Trans. Faraday Soc.,* **46,** 459 (1950).
17. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.,* **23** (1), 1 (1963).
18. Y. Ishida, M. Matsuo, S. Togami, K. Yamatuji, and A. Takayanagi, *Kolloid Z.,* **183,** 74 (1962).
19. H. K. Yip and H. L. Williams, *J. Appl. Polym. Sci.,* **20,** 1209, 1217 (1976).
20. G. Nemoz, J. F. May, and G. Vallet, *Angew. Makromol. Chem.,* **49,** 149 (1976).
21. S. Krause and N. Roman, *J. Polym. Sci. A,* **3,** 1631 (1965).
22. D. R. Paul and J. O. Altamirano, *Adv. Chem. Ser.,* **142,** 371 (1975).
23. T. Nishi and T. T. Wang, *Macromolecules,* **8,** 909 (1975).
24. R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.,* **16,** 593 (1976).