The Crystallization and Transition Behavior of Poly(vinylidene Fluoride) / Copoly(chlorotriofluorethylene-vinylidene Fluoride) Blends

A. SIEGMANN, G. COHEN and Z. BARAAM, *Department of Materials Engineering, Technion, Israel Institute of Technology, Haifa 32000, Israel*

Synopsis

Thermal analysis of solution precipitated blends of two crystallizable polymers, poly(vinylidene fluoride) (PVDF) and copoly(chlorotrifluorethylene-vinylidene fluoride) (copoly(CTFE-VDF)), has been carried out to study the transition temperatures, crystallinity, and crystallization rates. PVDF crystallizes over the whole blend composition either during precipitation from solution or upon cooling from the melt. The high degree of crystallinity attained, higher than in PVDF by itself, suggests the occurrence of partial PVDF-copolymer cocrystallization. The melt crystallization temperature, decreasing with cooling rate, is lower in PVDF-rich blends than for lean blends. However, the heat of crystallization increases with cooling rate, suggesting that the crystal composition depends on crystallization rate. No significant melting temperature depression due to blending was observed. However, the blends glass transition (T_g) changes linearly with composition, but less than expected by any mixing rule applicable to compatible systems. Annealing of the blends above T_g results in an additional crystalline phase consisting mainly of the copolymer. The amount of these crystals increases with PVDF content, due to partial cocrystallization and kinetic effects. The addition of the copolymer to PVDF results in a volume-filling spherulitic structure consisting of spherulites which decrease in size with increasing copolymer content.

INTRODUCTION

Crystallizable alloys, in which at least one of the components is crystallizable, are a unique class of polyblends which have recently attracted a lot of interest. The compatibility question in such blends is rather complex due to the existence of several phases. Blends of various types and degrees of compatibility were recently reported, including, for example, the following pairs: poly(vinyl chloride)/polycaprolactone (PVC/PCL),[1] poly(ethylene terephthalate)/polybutyleneterephthalate) (PET/PBT),[2] and poly(ethylene terephthalate)/polycarbonate (PET/PC),[3] polybutene-1/polypropylene (PB/PP),[4,5] and the most widely studied family of such blends consists of crystallizable poly(vinyledene fluoride) (PVDF) and poly(vinylacetate) (PVA),[6] poly(methyl methacrylate) (PMMA),[7-9] and poly(ethyl acrylate) (PEA).[10,11] PVDF was also found to be a compatibilizing agent in ternary mixtures of PMMA and PEMA, the latter being incompatible.[12] In blends consisting of PVDF, the latter partially crystallizes, depending on the blends' composition (PVDF content higher than 40–50%) and thermal history.[8,13] In general, the crystallization (T_c) and melting (T_m) temperatures of the PVDF are increasingly depressed with the admixing of increasing amounts of the other blend

CCC 0021-8995/89/061481-09$04.00

components.[8,13,14] The single glass transition temperature (T_g) of the compatible PVDF-containing blends changes linearly with composition;[8,13,14] in some systems the T_g remains constant in the blends' composition range which allows the PVDF to crystallize out.[13]

In the blends to be studied here, copoly(CTFE-VDF)/PVDE, both components are crystallizable (PVDF readily crystallizes[15] while copoly(CTFE-VDF) crystallizes only upon annealing from the amorphous state, or upon slow cooling from the melt[16]). Such two crystallizable polymers, when blended, can form mixed or separate crystals embedded in a compatible or incompatible amorphous phase. This pair of polymers has the potential to partially cocrystallize (the random copolymer, in the whole range of composition, crystallizes[17]), and to form a compatible amorphous phase, due to the common VDF monomer. Therefore, it is highly interesting to study the thermal transitions and the crystallization of copoly(CTFE-VDF)/PVDF blends of various compositions.

EXPERIMENTAL

A copolymer consisting of 72–77 mol% CTFE and 23–28 mol% VDF, Kel-F800 (Mw = 7.5×10^4, Mn = 2.9×10^4) supplied by the 3M Company (USA) and PVDF (Mw = 10^5) supplied by Polyscience Inc. (USA), were used throughout this study. Blends of various compositions were prepared by dissolving the desired amount of the two polymers in a common solvent, dimethylacetamide, followed by precipitation with ethanol. The blends were washed several times with ethanol and dried under vacuum, at 60°C. The effect of blends composition and thermal history on their crystallization, melting, and glass transition temperatures was studied using a Mettler TA-3000 differential scanning calorimeter (DSC) at a heating rate of 10°C/min and a temperature range of −60 to 200°C. The degree of crystallinity was calculated using 41.9[18] and 104.7 J/g[19] for the heat of fusion of totally crystalline copoly(CTFE-VDF) and PVDF, respectively. The reported melting temperatures are the endotherm peak temperatures and the glass transition was taken at the inflection point on the thermograms. The crystallization process of the blends was followed by holding the samples in the DSC at 200°C for 5 min followed by cooling at a controlled rate of 10°/min.

RESULTS

The thermal transitions of blends containing copoly(CTFE-VDF) and PVDF in the whole range of compositions were studied using DSC. Typical thermograms of as-prepared blends are shown in Figure 1. The DSC curve obtained for the copolymer (0% PVDF) exhibits no melting endotherm, as previously reported.[16] The T_g is identical to that measured for the bulk material,[16] indicating no solvent effect in the present samples. The melting temperature of the PVDF, 167°C, is consistent with literature.[20] The thermograms of as-prepared blends exhibit a single melting endotherm at temperatures just slightly lower than that of PVDF. The melting endotherm area, as presented by degree of crystallinity (Fig. 2), gradually increases with PVDF content. Interestingly, the crystallinity of the as-prepared samples (precipitated from solution) is significantly higher than that in samples which were quenched
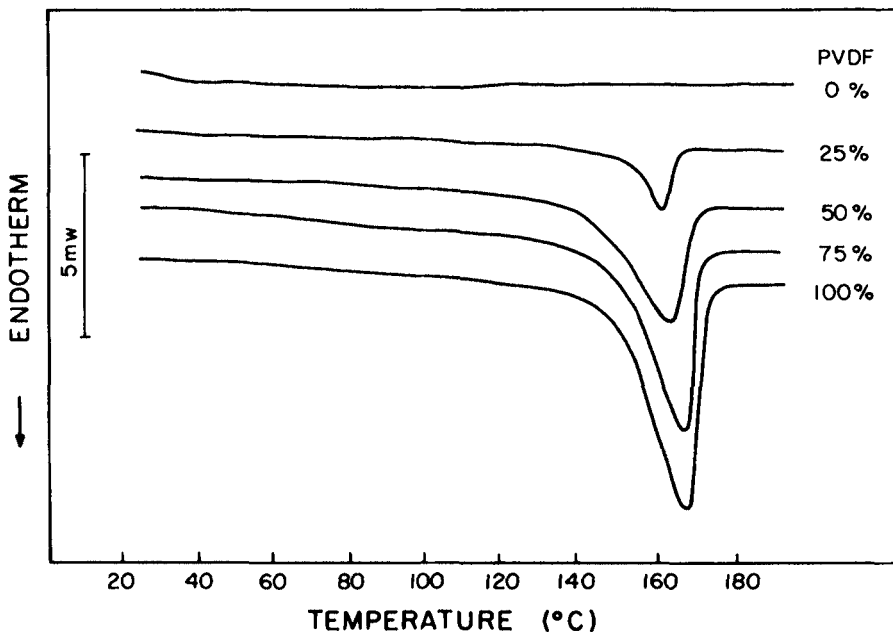
Fig. 1.   DSC thermograms of as prepared copoly(CTFE-VDF)/PVDF blends of various compositions (weight percent).

from the melt (held for 5 min at 200°C); no difference was observed in the melting temperature. Upon cooling the melt at a controlled rate of 10°C/min crystallization exotherm is observed (Fig. 3). The crystallization temperature of blends consisting of up to 35 wt% PVDF is approximately 148°C while that of blends rich in PVDF (> 65 wt%) is identical to the crystallization temperature of PVDF (135°C); the crystallization temperature gradually changes between these values in the intermediate blends composition (40–60 wt%).
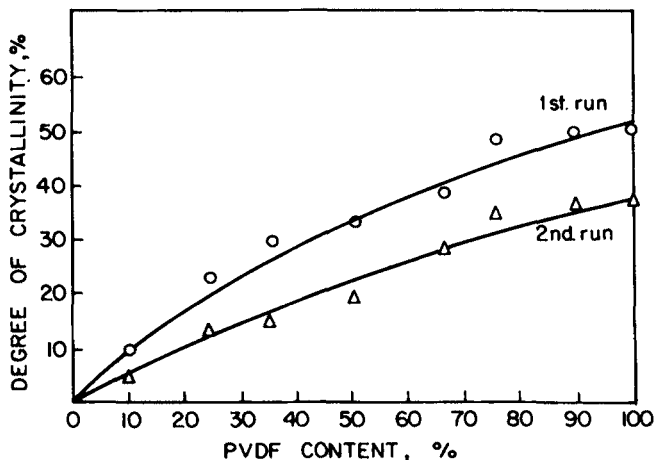

Fig. 2.   The effect of blends' composition on the degree of crystallinity, as prepared (○, 1st run) and after quenching from the melt (△, 2nd run).
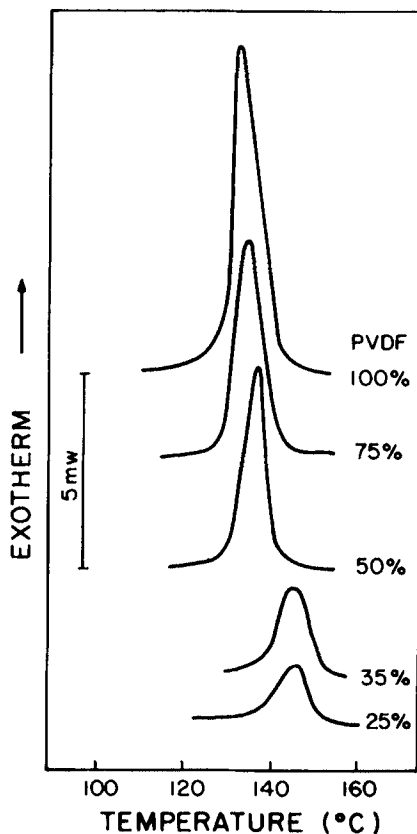
Fig. 3. Crystallization exotherms of various blends' compositions, obtained upon cooling in the DSC.

The effect of cooling rate on the crystallization process was studied using a blend consisting of 75 wt% PVDF; the crystallization temperature decreases while the heat of crystallization increases with increasing cooling rates. The single glass transition temperature of blends consisting of up to 50% PVDF (T_g is not clearly observable at higher PVDF contents) linearly decreases with increasing PVDF content (Fig. 4). However, the measured values are higher than those predicted by the Fox rule of mixing[21] (T_g of PVDF is $-40°C$[20]).

To study the effect of annealing on the crystallization of the blends, two representative compositions (10 and 25 wt% PVDF) were chosen. They were annealed for up to 30 days at 55°C, which is the temperature at which the copoly(CTFE-VDF) crystallizes at the highest rate.[16] The thermograms of such annealed blends exhibit two endotherms at 85–90°C, corresponding to the copolymer, and 167–170°C, corresponding to PVDF. The range of temperatures quoted is a result of increasing melting temperature with annealing time. Upon melting and quenching in the DSC, so called second run, only the higher temperature melting endotherm is observed, the area of which is much smaller than in the first run. The degree of crystallinity was calculated separately (1st run) for the crystals which melt at the two temperatures, assuming the heat of fusion of the separate blend components. As seen in
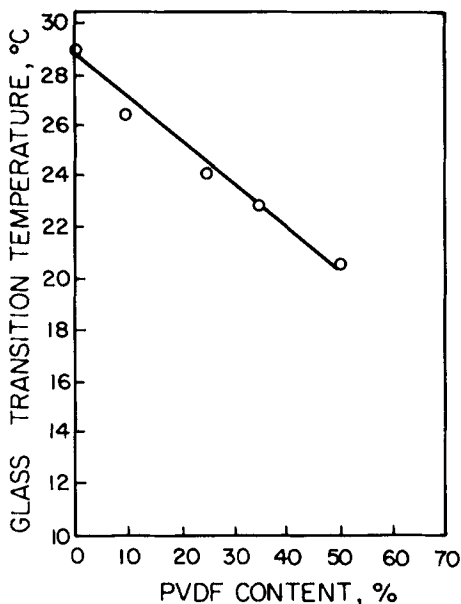
Fig. 4.   The glass transition temperature as a function of the blends' composition.

Figure 5(a), the crystallinity of the higher melting crystals in the as-prepared blends, consisting of 10 and 25 wt% PVDF, is surprisingly high, 10 and 23%, respectively. In the 10 wt% PVDF blend the degree of crystallinity continues to increase gradually even upon annealing at 55°C, while in the 25 wt% PVDF blend the crystallinity remains practically unchanged. The lower melting endotherm is only observed for the studied blends which were annealed for at least 3 days. The crystallinity of the lower melting crystals in the 10 wt% PVDF blends is always lower than that observed in the copolymer by itself. However, in the 25 wt% PVDF blends this crystallinity is always higher than in the 10 wt% PVDF blends and higher than that in the copolymer only after 10 annealing days [Fig. 5(b)]. It should be mentioned that the T_g's of these blends are not affected by the annealing at 55°C.

The morphology of the blends was studied using optical microscopy. The only clear observation is the marked reduction in the PVDF spherulitic size with increasing copolymer content. The as-prepared blends consist of spherulites about 100, 15, and 5 μm (average values) in diameter in systems containing 100, 75, and 25 wt% PVDF, respectively. In the latter, in spite of the low degree of crystallinity (23%) the spherulitic structure still fills the whole material volume.

DISCUSSION

The blend of copoly(CTFE-VDF) and PVDF was found to be a rather complicated, unusual, and interesting system, which exhibits partial compatibility both in the crystalline and amorphous phase. PVDF crystallizes over the whole blends' composition range, different from other PVDF blends. In PVDF blends with, for example, PMMA and PEMA,[8] crystallization occurs only in blends consisting of at least 40–50 wt% PVDF. The degree of
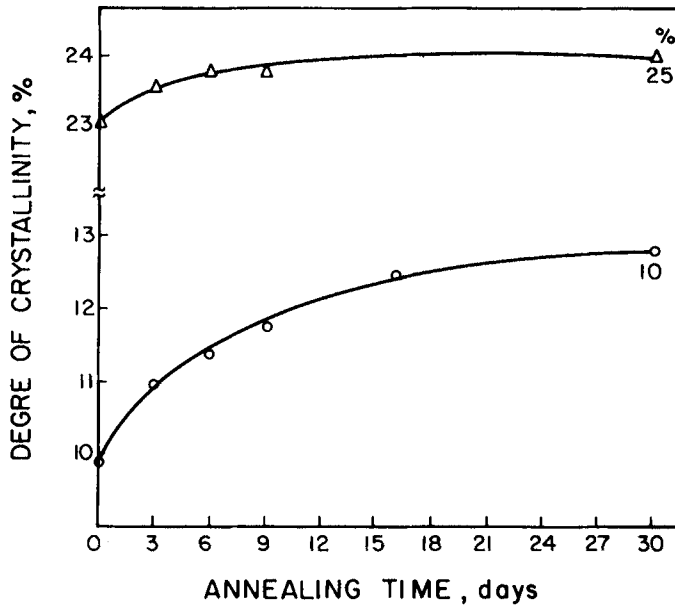
(a)
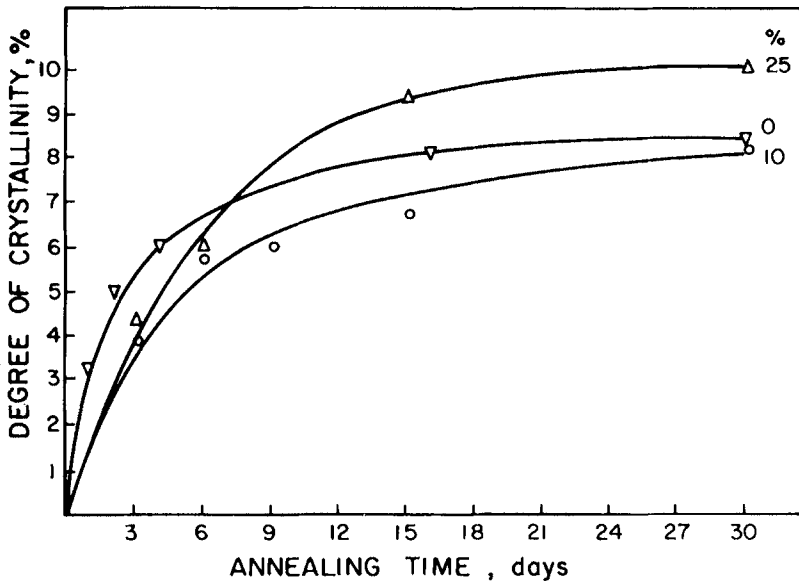
(b)

Fig. 5. Crystallization isotherms of copoly(CTFE-VDF)/PVDF blends consisting 0 ($\triangledown$), 10 ($\bigcirc$) and 25 ($\triangle$) wt% PVDF based on the endotherm at 167°C (a) and 85°C (b).

crystallinity (T_m corresponds to PVDF) is higher than expected according to the PVDF content, contrary to the well known lowering of a polymer crystallinity when blended.[22] For example, in a 10 wt% PVDF blend the crystallinity is 9.9% whereas, based on the PVDF crystallinity alone (53%), the expected crystallinity in this blend should be only 5.3%. It is thus speculated, based on the crystallizability of the copolymer itself,[6] that the two blend-crystallizable components partially cocrystallize. Moggi et al.[17] have demonstrated that random CTFE-VDF copolymers, in the whole range of composition, crystallize; the unit cell dimensions and degree of crystallinity depend on the copolymer composition. In the presently studied blends, the amount of cocrystalized copolymer was estimated, assuming a constant contribution of PVDF to the crystallinity, relative to its content (content × 53%) however, independent on the blend composition. As seen in Figure 6, in blends containing up to about 40 wt% PVDF, the copoly(DTFE-VDF) makes about a third of the total cocrystallized material. In PVDF-rich blends, the crystallization ratio gradually decreases with increasing PVDF content. In blends lean in PVDF, the latter crystallizes out of a compatible blend (probably a solution) at a relatively low rate,[8] enabling cocrystallization. The amount of cocrystallized copolymer increases in these blends with the content of PVDF available for cocrystallization. However, in PVDF-rich blends the crystallization rate becomes high approaching that of PVDF by itself, as is also expressed by the PVDF crystallization temperature (Fig. 3), limiting the cocrystallization process. It should be mentioned here that the cocrystallization data (Fig. 6) are all underestimated since the PVDF crystallizes in blend to a lesser degree than by itself (the base of 53% crystallinity is too high).[13] It is also quite interesting to note that the ultimate cocrystallization is limited
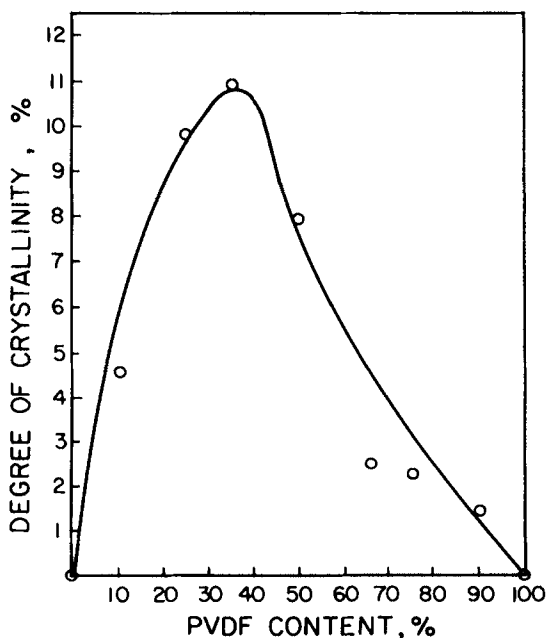

Fig. 6. Percent crystallinity contributed by the copolymers to the total crystallinity in the as prepared blend.

to results in crystalline phase containing a high VDF/CTFE ratio such that PVDF unit cell dimensions are only slightly distorted.[17]

The crystallization temperature is unexpectedly higher in blends of low PVDF content than for PVDF by itself, contrary to other PVDF blends such as PVDF/PMMA[8] (PMMA is however an amorphous polymer). The copolymer at such crystallization temperatures is still above its melting temperature, acting as a liquid diluent for the crystallizing PVDF and thus may enhance the latter's crystallization rate. As with any crystallizable polymer, the depression of crystallization temperature with increasing cooling rate is an expected kinetic effect. However, the simultaneous rise in the heat of crystallization is contrary to the behavior of other PVDF blends.[8] It is suggested that this increase in the heat of crystallization is not due to increasing crystallinity but rather to the crystals' composition (degree of cocrystallization). At low cooling rates, a greater degree of PVDF copolymer cocrystallization is possible, resulting in less ordered crystals than formed at high cooling rates, when it is likely that less cocrystallization occurs. Therefore, the heat of crystallization decreases with increasing amount of cocrystallized copolymer.

Interestingly, the melting temperature of the cocrystals is not significantly lower than that of PVDF, which is contrary to the melting temperature depression observed in other PVDF blends.[8,13] This composition- (of both crystalline and amorphous phases) independent melting temperature is probably the result of two opposing effects, namely melting temperature depression effects[8,13] and strong intermolecular forces acting in the cocrystal.

The glass transition of blends containing less than 50 wt% PVDF decreases linearly with increasing PVDF content, indicating the formation of a compatible amorphous phase. However, the T_g depression is not as deep as predicted for miscible blend systems by the weight- or volume-averaging procedures.[13,21-23] The T_g depression does not follow such predictions even if the composition is corrected for the fractions which crystallize out. Such deviations were reported for other PVDF blends [e.g., Ref. 13]. It is difficult even to speculate on the blends' structure according to the T_g dependence on composition, since the T_g of PVDF was not presently measured and the values, quoted in the literature are rather scattered and still being debated.[13,23-27]

Annealing of blends at 55°C does not affect their T_g, however, it enables crystallization of the copoly(CTFE-VDF) ($T_m = 85-90°C$) without significantly affecting the PVDF crystalline phase. Interestingly, the ultimate copolymer crystallinity in a blend containing 25 wt% PVDF is higher than in a blend containing 10 wt% PVDF and in the copolymer by itself. This observation is attributed either to some cocrystallization of PVDF in the copolymer crystals or to the presence of PVDF crystals, which act as a nucleating agent for the copolymer. It is presently not possible to distinguish between these effects.

SUMMARY

Blends in which both components are crystallizable and highly compatible are unique in their complicated behavior and are different in several respects from crystalline/amorphous mixtures. The presently studied copoly(CTFE-VDF)/PVDF blends are miscible both in the melt and the amorphous state. The PVDF crystallizes in blends of all compositions either during precipita-

tion from the blends' solutions or upon cooling from the melt. Moreover, the crystals which melt at the PVDF melting temperature may actually be cocrystals, consisting of chains of both blends' components. The crystallization temperature, upon cooling from the melt, in blends rich in PVDF is unexpectedly lower than in blends consisting of less than 35 wt% PVDF. This simultaneous increase of the crystallization temperature and the heat of crystallization with increasing the crystallization rate, suggests the dependence of cocrystals composition on the cooling rate.

While no significant melting temperature depression was observed upon blending, contrary to the commonly reported depression in crystalline blends, the glass transition was found, as expected, to shift linearly with composition, though not as predicted for miscible blends. Annealing of the blends above their T_g enables the formation of an additional crystalline phase which consists mainly of copoly(CTFE/VDF). The fraction of this phase increases with PVDF content in the blend, being even higher than the degree of crystallinity obtained in the copolymer by itself.

References

1. J. V. Kolske, and R. D. Lundberg, *J. Polym. Sci.,* Part A-2, **7**, 795 (1969).

2. R. S. Stein, F. B. Khambatta, F. P. Warner, T. Russell, A. Escala, and E. Balizer, *J. Polym. Sci., Polym. Symp.,* **63**, 313 (1978).

3. R. L. Jalbert, in *Modern Plastics Encyclopedia,* A. Arganoll, Ed., McGraw-Hill, New York, 1975, p. 109.

4. A. Siegmann, *J. Appl. Polym. Sci.,* **24**, 2333 (1979).

5. A. Siegmann, *J. Appl. Polym. Sci.,* **27**, 1053 (1982).

6. R. E. Bernstein, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.* **18**, 683 (1978).

7. J. S. Noland, N. N. C. Hsu, R. Saxon, and J. M. Schmitt, *ACS Adv. Chem.,* **99**, 15 (1971).

8. T. Nishi and T. T. Wang, *Macromolecules,* **8**, 909 (1975).

9. E. Roerdink and G. Challa, *Polymer,* **21**, 1161 (1980).

10. D. C. Wahrmund, R. E. Bernstein, J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.,* **18**, 677 (1978).

11. R. M. Briber and F. Khoury, *Polymer* **28**, 38 (1987).

12. T. K. Kwei, H. L. Frisch, W. Rdigan, and S. Vogel, *Macromolecules,* **10**, 157 (1977).

13. R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.,* **16**, 593 (1976).

14. D. R. Paul and J. O. Altamirano, *ACS Adv. Chem.,* **142**, 371 (1975).

15. C. Mancarella and E. Martuscelli, *Polymer,* **18** 1240 (1977).

16. A. Siegmann, G. Cohen, and Z. Baraam, to be published.

17. G. Moggi, P. Bonardelli, and J. C. J. Bart, *J. Polym. Sci., Polym. Sci. Ed.,* **22**, 357 (1984).

18. W. E. Cady, and L. E. Caley, Properties of Kel F-800 Polymer, T. R., Lawrence Livermore Laboratory, University of California.

19. S. S. Shalaby, *Thermal Characterization of Polymeric Materials,* E. A. Turi, eds., Academic Press, New York, 1981.

20. D. W. Van Krevelan, *Properties of Polymer,* Elsevier Science Publishing Co., Amsterdam, 1976.

21. S. Krause and J. Roman, *J. Polym. Sci.,* Part A, **3**, 1631 (1965).

22. E. Martuscelli, R. Palumbo, and M. Kryszewsky, *Polymer Blends,* Plenum Press, New York, 1979.

23. J. S. Noland, N. N. C. Hsu, R. Saxon, and J. M. Schmitt, *ACS Advan. Chem. Ser.,* **99**, 15 (1971).

24. S. Osabi and Y. Ishida, *J. Polym. Sci., Polym. Phys.,* **12**, 1717 (1974).

25. N. Nakagawa and Y. Ishida, *Kalloid Z.,* **251**, 103 (1973).

26. T. K. Kwei, G. D. Patterson, and T. T. Wang, *Macromolecules,* **9**, 780 (1976).

27. M. Galin, *Makromol. Chem., Rapid Commun.,* **8**, 411 (1987).