Modification of Chlorinated Poly(vinyl chloride) by Blending with Epoxidized Polybutadiene

DIONISSIA D. SOTIROPOULOU, KOSTAS G. GRAVALOS, and NIKOS K. KALFOGLOU*

Department of Chemistry, University of Patras, 26110 Patra, Greece

SYNOPSIS

The compatibility of epoxidized poly(cis-1,4-butadiene) (EPB) with chlorinated polyvinylchloride (CPVC) was investigated. Blends studied covered the complete composition range using EPB at two degrees of epoxidation: 20 and 43 mol % oxirane units. Tensile properties of EPB(63)/CPVC were also studied at the 50/50 composition. Dynamic mechanical analysis (DMA) showed that both sets of blends were miscible at the segmental level except for the rich CPVC compositions. All blends showed good tensile properties, even those where DMA indicated phase separation. This may be attributed to strong segmental interactions of the donnor–acceptor type between the oxirane and acidic-hydrogen-containing groups of these complementary dissimilar blend partners.

INTRODUCTION

Diversification of the properties of thermoplastics may be attained most inexpensively by blending with a low T_g component. If the latter is a polymer, depending on the degree of compatibility, one obtains a miscible blend with properties intermediate between those of its constituents, or a phase separated system whose properties are an additive combination of the properties of its components.[1] The latter systems are by no means of lesser importance as long as there is good adhesion between phases. In fact, certain properties (e.g., impact strength) may best be obtained with heterogeneous blends.[2] Often it is possible to obtain both types of blends by varying the ratio of the two components and this has been observed in several blends involving epoxidized polyhydrocarbons/chlorinated polymers.[3–6] Thus, it was determined that the parameter controlling the degree of compatibility was the ratio (oxirane)/(CHCl) moieties in the blend. It was also discovered that though the blends were immiscible at certain compositions their tensile properties did not suffer–a fact that may be attributed to strong interactions

between the oxirane unit and the proton donating group of the complementary dissimilar partners.

In this work we report on the modification of chlorinated poly(vinylchloride) (CPVC) properties by blending CPVC with epoxidized poly(cis-1,4 butadiene) (EPB) at two degrees of epoxidation. CPVC, due to its higher chlorine content, has a higher T_g and rigidity than PVC. This would allow us to obtain a broader spectrum of properties and also to examine whether the higher concentration of proton donors (e.g., —CHCl—) would enhance miscibility or require increased oxirane contents in EPB to attain it. In the case of PVC/EPB blends it was found that at oxirane levels of approximately 43 mol %, blends were semicompatible, complete miscibility requiring a higher degree of epoxidation (> 50 mol %).[5] Such a high concentration of oxirane units is undesirable as it raises the T_g of the modifier (EPB), thus reducing its plasticizing efficiency.

In previous work on CPVC modification the effect of the $(CH_2)/(COO)$ ratio on miscibility was studied in blends of aliphatic polyesters and poly(ϵ-caprolactone)[7] and in blends with aromatic polyesters.[8] Shiomi et al. investigated the applicability of copolymer–copolymer miscibility theory using blends with poly(ethylene-co-vinyl acetate).[9]

Other related work includes the studies of Prud'homme and coworkers on the miscibility of

---

PVC/CPVC using PCL as a compatibilizer,[10] and on the relative miscibility of poly(ethylene-co-caprolactone) with CPVC, PVC, and chlorinated polyethylene (CPE).[11]

EXPERIMENTAL

Materials—Preparation and Characterization

PB with approximately 90% cis-1,4 structure was purified by dissolution in chloroform followed by precipitation in methanol. It had a M_w of 2.5×10^5. CPVC was a product of Atochem Co. (France). GPC analysis in tetrahydrofuran gave $M_n = 52,900$ and a polydispersity index $I = 1.84$. Chlorine content obtained by elemental analysis was 64.3 wt %.

Epoxidation of unsaturated polymers[12] and of PB has been reported before.[5,13] The method applied in this study employed a peracetic acid solution using the following procedure. Glacial acetic acid was stirred at room temperature with a 50 wt % hydrogen peroxide solution at a mole ratio of 2 to 1, respectively, in the presence of 1 wt % concentrated sulfuric acid. Analysis of the reaction products after a period of 24 h gave 26 wt % peracetic acid and 8 wt % hydrogen peroxide.[14]

To prepare EPB, a solution of 5.4 g PB (0.1 mol C=C) in 108 mL chloroform was cooled to 5°C, and under constant gentle stirring 15 mL (0.05 mol) of peracetic acid was added. Subsequently, the sulfuric acid in the mixture was neutralized with $4N$ sodium hydroxide solution. The temperature was kept at 5°C and the progress of epoxidation was followed by sampling at intervals and determining with ¹H NMR the ratio of the resonance peak area of oxirane (2.8 ppm) and ethylenic (5.2 ppm) hydrogens. Epoxidation was terminated with the addition of 100 mL H₂O, removal of the aqueous phase, washing the chloroform phase with dilute sodium carbonate solution, and, after concentrating it by solvent evaporation, precipitating the dissolved EPB in excess methanol. The advantages of using peracetic acid versus performic acid[5] are shorter epoxidation time and a reaction proceeding in homogeneous phase. Figure 1 gives the degree of PB conversion with time. IR analysis did not indicate any OH absorbance due to hydrolyzed product (3430 cm⁻¹) or furan ring formation (1067 cm⁻¹). For the EPB samples below the degree of epoxidation is shown in parentheses following EPB.

Blends were prepared by dissolving in a common solvent THF and casting in Teflon coated pans. Films were dried in a vacuum oven at 50°C to constant weight (ca. 1 week).
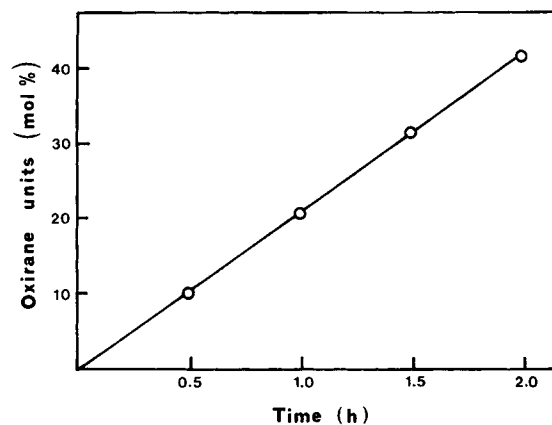

Figure 1   Degree of PB conversion with time at 5°C.

Apparatus and Procedures

Dynamic viscoelastic data (E^*) and $\tan\delta$ were determined at 110 Hz using a direct reading viscoelastometer (Rheovibron Model DDV II-C, Toyo Baldwin) and the procedure previously described.[3] Specimen dimensions were $3 \times 0.3 \times 0.08$ cm³. Data were obtained at 3°C intervals, and duplicate runs were made on phase-separated blends. To test whether thermally induced phase separation takes place, measurements on phase-separated blends were obtained with thermal recycling.

Differential scanning calorimetry measurements were performed with a DuPont 910 calorimeter coupled with a 990 programmer recorder. Calibration was made with an Indium standard. Sample weight was approximately 20 mg and scanning rate 10 deg min⁻¹. The T_g data obtained were invariably lower than those determined using the DMA technique by approximately 10°C. This can be attributed to a frequency shift.

Tensile tests were performed according to ASTM D882 at room temperature using a J. J. Tensile Tester Type T5001 and film strips measuring $6.0 \times 1.20 \times 0.08$ cm³.

RESULTS AND DISCUSSION

EPB(20)/CPVC Blends

Figure 2 gives the dynamic mechanical spectra in terms of loss E'' and storage E' modulus. The former indicate that immiscibility sets in at high CPVC contents, approximately 75 wt %. Though immiscible, the 25/75 composition is not separated into pure component phases since no relaxations at −78°C for EPB(20) and 102°C for CPVC were de-
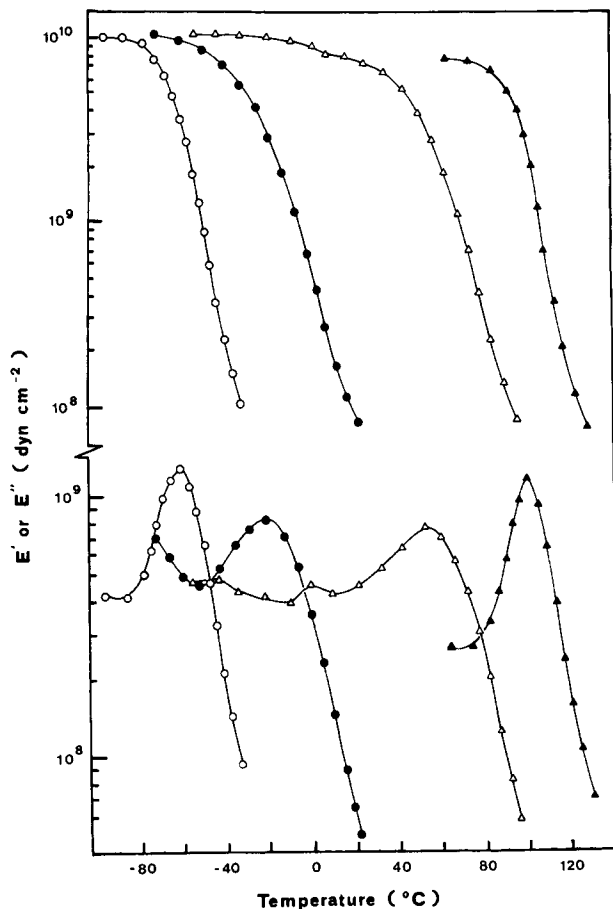
Figure 2 Thermomechanical spectra of EPB(20)/ CPVC blends: (○) 75/25; (●) 50/50; (△) 25/75; (▲) 0/ 100. For clarity not all experimental points are included.

tected. This is evidence for strongly interacting components giving two coexisting mixed phases— one with a high proportion of EPB(20) and another

with a high content of CPVC, having T_g at 0°C and 53°C, respectively. Further indication of the good adhesion of the semicompatible composition (25/ 75) is provided by the good tensile properties of the blend. True stress–strain and ultimate properties are summarized in Figures 3 and 4, respectively. Due to high specimen extensibility, engineering stress was converted to true-stress assuming affine deformation. This gives a more realistic assessment of tensile stress for most compositions. In Figure 3 stress–strain curves are characteristic of the transition from elastic to ductile to plastic behavior at high CPVC contents. The same figure includes data on EPB(65)/CPVC for the 50/50 composition to demonstrate the stiffening effect of polarity at increased levels of epoxidation for the same CPVC content. Ultimate properties are summarized in Figure 4. If engineering stress is converted to true ultimate stress one obtains the intermediate composition as the optimum in terms of tensile strength. Though impact strength was not determined, it is reasonable to expect that the good adhesion of the rubbery component onto the thermoplastic resin at phase separated compositions containing low rubber contents would enhance this property;[2] the significant width of the corresponding relaxation spectrum[15] attests to this (see Fig. 2, composition 25/75).

EPB(43)/CPVC Blends

DMA data are summarized in Figure 5. In this system miscible compositions are obtained at CPVC contents < 90 wt %. Again the phase separated composite blend 10/90 has two relaxations with maxima at 69°C and 97°C. As in the previous case
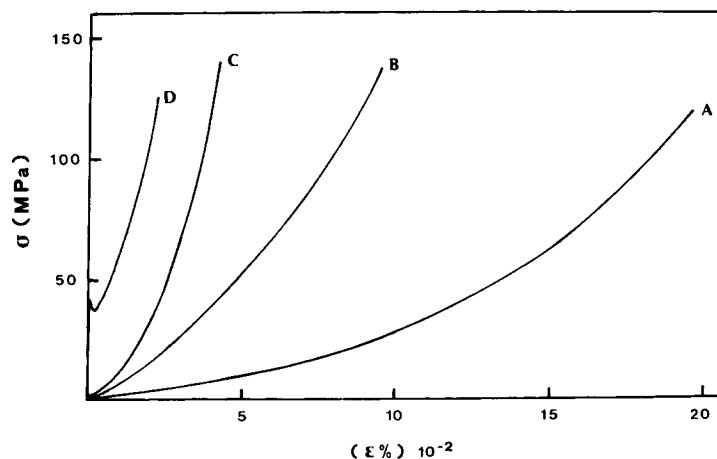

Figure 3 True stress–strain properties of EPB(20)/CPVC blends: A 75/25; B 50/50; D 25/75. EPB(65)/CPVC blend: C 50/50.
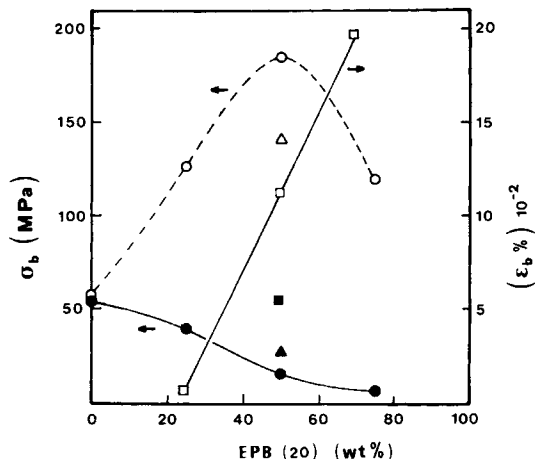
Figure 4 Ultimate properties of EPB(20)/CPVC blends: (- ● -) nominal σ_b; (- O -) true σ_b; (- □ -) ϵ_b. EPB(65)/CPVC, 50/50 blend: (▲) nominal σ_b; (△) true σ_b; (■) ϵ_b.

the good adhesion of phases and the existence of secondary relaxations is expected to contribute to energy dissipating mechanisms and thus to increase impact strength.

Tensile properties in Figure 6 already show the appearance of ductile yielding for the 50/50 composition. This is more clearly shown for the 25/75 blend where cold drawing sets in. On the basis of tensile behavior, blends fall into two groups. At CPVC contents < 50 wt %, blends are highly elastic; at high CPVC levels plastic behavior predominates. These findings differentiate the EPB(43) blends from the previous system. Ultimate properties reported in Figure 7 show that elongation levels off at high rubber contents, and strength at high CPVC compositions. It is of practical significance that the strength of the mixed phase blend 10/90 is not impaired by phase separation. The diversification of tensile properties indicated by the stress–strain behavior is also indicated when true–ultimate stress is plotted versus composition in Figure 7. The "binodal" curve obtained differentiates between blends with low and high contents of CPVC and supports the view that a different reinforcing mechanism is operative in the two sets of composites which correspond to miscible and marginally miscible composite phase blends.

A qualitative measure of blend component interactions may be obtained from the T_{gb} dependence on composition.[16,17] This is given in Figures 8 and 9 for the miscible compositions of the EPB(20)/CPVC and EPB(43)/CPVC blends, respectively. Several equations have been proposed to correlate

the T_{gb} composition dependence. We tested the simple Fox relationship[18]

$$1/T_{gb} = W_A/T_{gA} + W_B/T_{gB} \qquad (1)$$

the Gordon–Taylor equation[19]

$$T_{gb} = T_{gA} + kW_B(T_{gB} - T_{gA})/W_A \qquad (2)$$

and the Kwei relationship[20]

$$T_{gb} = (W_A T_{gA} + kW_B T_{gB})/(W_A + kW_B) + qW_A W_B \qquad (3)$$

In the above equations, W_i and T_{gi} are the weight fractions of component i and its T_g, respectively; k
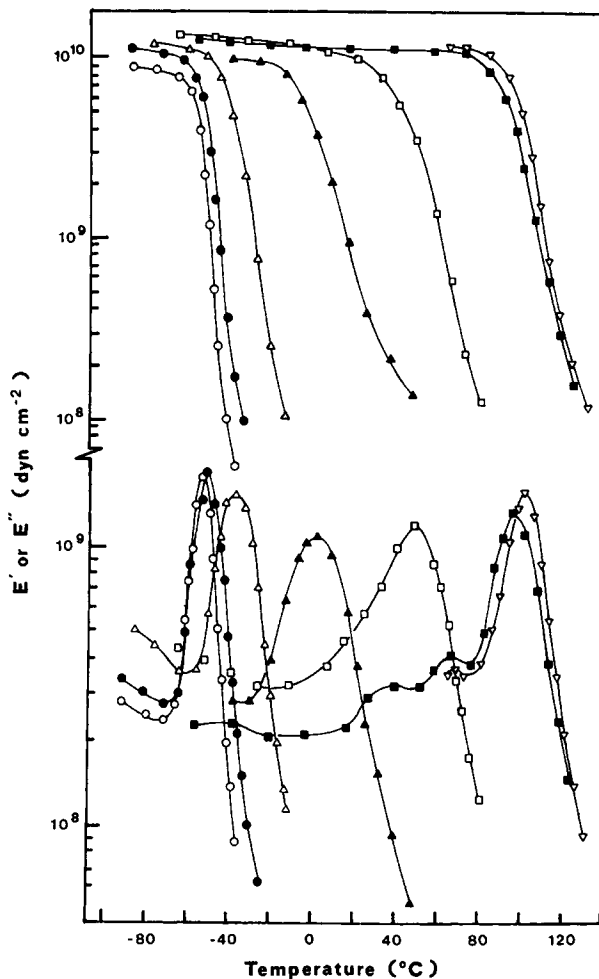

Figure 5 Thermomechanical spectra of EPB(43)/ CPVC blends: (O) 100/0; (●) 90/10; (△) 75/25; (▲) 50/ 50; (□) 25/75; (■) 10/90; (▽) 0/100. For clarity not all experimental points are included.
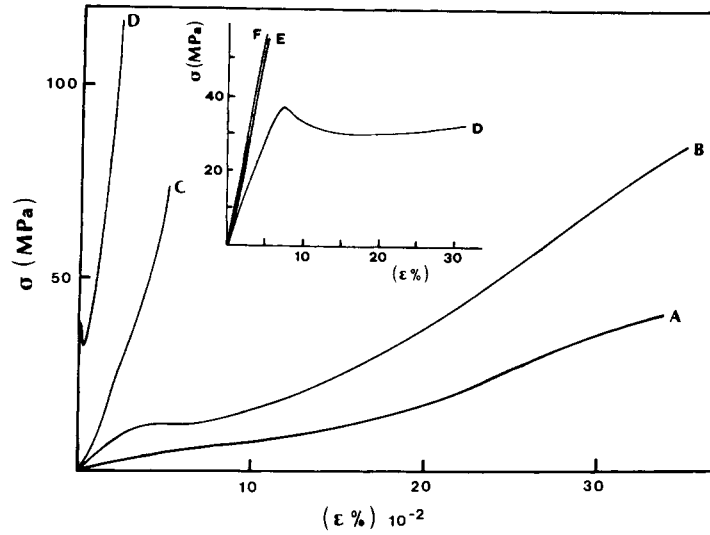
Figure 6 True stress–strain properties of EPB(43)/CPVC blends: A 90/10; B 75/25; C 50/50; D 25/75; E 10/90; F 0/100.

is a constant shown subsequently to be the ratio of the volume expansion coefficient difference in the viscoelastic and glassy states of the two homopolymers. The parameter q determining the magnitude of the product $W_A W_B$ gives, according to Kwei,[21] an overall measure of the specific interactions in a blend. Analysis of T_{gb} data by various workers indicate that though q is not descriminating between interactions from monomers of the two blend partners or belonging to the homopolymer, its absolute magnitude gives an estimate of proton donnor–acceptor interactions. In the present system these originate from the oxirane unit (proton acceptor) and the α and β acidic hydrogens of CPVC.

A least squares analysis of the data using the above equations showed that most successful in predicting T_{gb} was that of Kwei, followed by those of Gordon–Taylor and Fox.
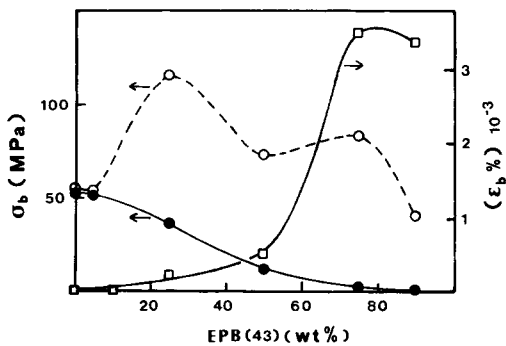
The parameters obtained using Kwei's equation

were $k = 1.0$, $q = -114$ for EPB(43)/CPVC and $k = 1.0$, $q = -135$ for EPB(20)/CPVC blends.

With the Gordon–Taylor equation, $k = 0.55$ and $k = 0.41$ for the above blends, respectively. The T_{gb} predicted using the Fox relation is also depicted in Figures 8 and 9. The k data obtained with Eq. (2) and by analogy to polyester–chlorinated polymer miscible pairs[22] suggest that interaction increases with the degree of epoxidation. Moreover, the set of values obtained using Kwei's equation[17] indicates a significant local alignment of chains for the
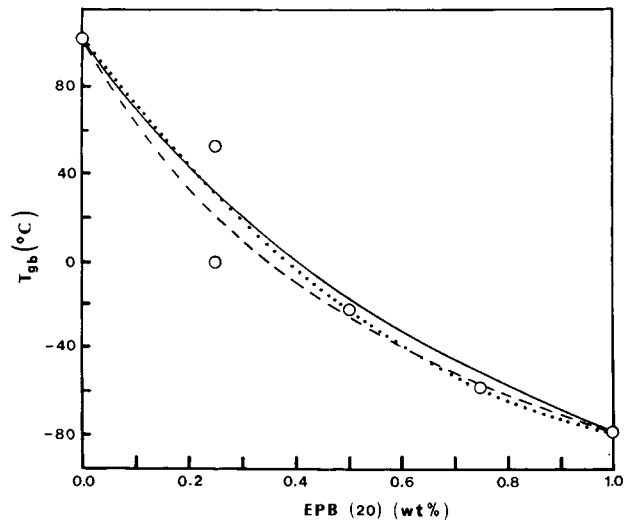

Figure 7 Ultimate properties of EPB(43)/CPVC blends: (- ● -) nominal σ_b; (- O -) true σ_b; (- □ -) ϵ_b.

Figure 8 T_{gb} composition dependence of EPB(20)/CPVC blends. Theoretical prediction according to equations of Fox (———), Gordon-Taylor (- -); Kwei (· · ·). Pure EPB(20) data taken from Ref. 5 (DMA data).
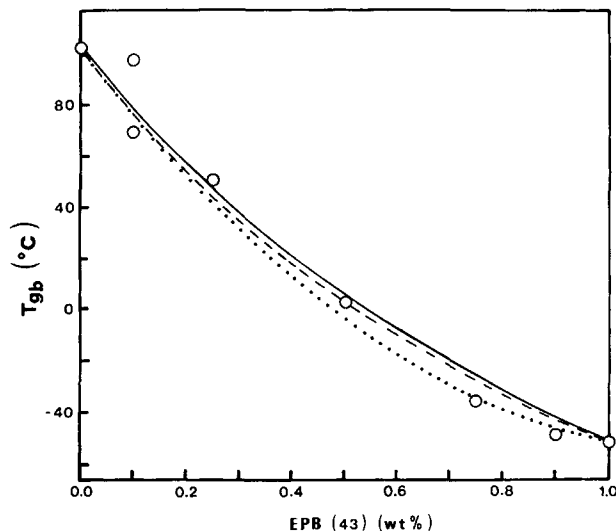
Figure 9 T_{gb} composition dependence of EPB(43)/CPVC blends. Theoretical prediction according to equations of Fox (——), Gordon-Taylor (- -); Kwei ($\cdot\cdot\cdot$) (DMA data).

EPB(43)/CPVC blends and the existence of two molecular morphologies or two states with different degrees of backbone stabilization for the EPB(20)/CPVC system.

CONCLUSIONS

To conclude, EPB epoxidized to an adequate level (45 mol %) gives miscible blends with CPVC. Depending on the degree of EPB epoxidation a blend composition-dependent immiscibility is observed, higher CPVC contents requiring increased levels of EPB epoxidation. This has been observed also in analogous blends previously studied, e.g., epoxidized natural rubber (ENR)/PVC, ENR/CPE, and EPB/PVC.[3,4,5]

At high CPVC compositions semicompatible blends are obtained having good tensile properties. This may find important applications in the impact modification of CPVC and other chlorinated plastics.

REFERENCES

1. L. A. Utracki, *Int. Polymer Processing*, **1**, 2 (1987).
2. S. Newman, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 2, Chap. 13.
3. A. G. Margaritis and N. K. Kalfoglou, *Polymer* (London), **28**, 497 (1987).
4. A. G. Margaritis, J. K. Kallitsis, and N. K. Kalfoglou, *Polymer* (London), **28**, 2123 (1987).
5. A. G. Margaritis and N. K. Kalfoglou, *Eur. Polym. J.*, **24**, 1043 (1988).
6. A. G. Margaritis, J. K. Kallitsis, and N. K. Kalfoglou, *Polymer* (London), **30**, 2253 (1989).
7. G. Belorgey, M. Aubin, and R. E. Prud'homme, *Polymer* (London), **23**, 1051 (1982).
8. M. Aubin and R. E. Prud'homme, *Polym. Eng. Sci.*, **24**, 350 (1984).
9. T. Shiomi, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **19**, 2644 (1986).
10. B. Ameduri and R. E. Prud'homme, *Polymer* (London), **29**, 1052 (1988).
11. D.-Z. Ma and R. E. Prud'homme, *Polymer* (London), **31**, 917 (1990).
12. D. Swern, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley-Interscience, New York, 1967, Vol. 6, p. 83.
13. D. Zuchowska, *Polymer* (London), **21**, 514 (1980); **22**, 1073 (1981).
14. D. Swern, in Organic Reactions, R. Adams et al., Eds., Wiley, New York, 1953, Vol. 7, p. 392.
15. H. Keskkula, R. F. Boyer, and S. C. Turley, *J. Appl. Polym. Sci.*, **15**, 351 (1971).
16. M.-J. Brekner, H. A. Schneider, and H.-J. Cantow, *Polymer* (London), **29**, 78 (1988).
17. A. A. Lin, T. K. Kwei, and A. Reiser, *Macromolecules*, **22**, 4112 (1989).
18. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
19. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
20. T. K. Kwei, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 307 (1984).
21. J. R. Pennacchia, E. M. Pearce, T. K. Kwei, B. J. Bulkin and J.-P. Chen, *Macromolecules*, **19**, 973 (1986).
22. R. E. Prud'homme, *Polym. Eng. Sci.*, **22**, 90 (1982).