Polymer Journal, Vol. 31, No. 7, pp 563—568 (1999)

Thermal and Phase Behavior of Polyurethane Based on Chain Extender, 2,2-Bis-[4-(2-hydroxyethoxy)phenyl]propane

Tae Won SON,† Dong Won LEE, and Sang Kyoo LIM

School of Textiles, Yeungnam University, Kyungsan 712–749, Korea

(Received September 7, 1998)

ABSTRACT: A series of polyurethanes based on Poly(oxytetramethylene)glycol (PTMG), 4,4′-diphenylmethane diisocyanate (MDI) and 2,2-bis-[4-(2-hydroxyethoxy)phenyl]propane (BHPP) was synthesized by two-step solution polymerization varying PTMG soft segment length and hard segment content. Thermal and dynamic mechanical properties were studied by DSC and DMA. Solubility and interactions were calculated and quantitative assessment based on the shift of glass transition temperature and heat capacity change at glass transition was used to predict the extent of phase separation. DSC and DMA results showed that T_g shifted to higher temperature with increasing hard segment content and decreasing soft segment molecular weight, indicating partial phase mixing between hard and soft segment.

KEY WORDS Phase Separation / Solubility Parameter / Interaction Parameter / Differential Scanning Calorimetry / Dynamic Mechanical Analysis /

Most segmented polyurethanes are prepared with a two-step method where the polyol is end-capped with excess diisocyante, followed by chain extension with stoichiometric amount of chain extender. In the final polymer the hard and soft segments tend to segregate, due to thermodynamic immiscibility between hard and soft segments, and produce a phase separated morphology of hard segment-rich and soft segment-rich phase. Phase separation is of primary importance, since it strongly affects the properties and gives rise to the interesting and useful properties of these materials. It is desirable that there is always chance of partial phase separation, but at the phase boundaries there is always chance of partial phase mixing.[1–4]

Phase mixing is quite complex, and much theoretical work has been done in order to predict the behavior of the components in the mixture.[5] One simple method of predicting phase compatibility is based on the composition of solubility parameters δ of both phases and calculation of interaction parameter χ. Using the group contribution method and tabulated values for the molar attraction constants, solubility for both phases can be calculated. It should be pointed out that crystallization of one of the phases introduces additional incompatibility in the system. Various experimental methods have been used for assessment of the extent of phase separation, such as mechanical and dielectric measurements, SAXS, SANS, and DSC. Phase mixing decreases the tensile modulus, causes shift of the onset of a sudden drop in E' or E'' and maximum in the tan δ relative to the same properties of the reference material of known degree of phase separation. DSC is most promising, since it is accurate and measurements are relatively easy. The degree of phase separation may be measured by heat capacity at T_g and the shift of T_gs of the soft and hard segments. The heat capacity, ΔC_p, at the glass transition has been applied to the study of segmented polyurethanes.[6,7]

Relative polarity(solubility parameters) of hard and soft block components influence the microstructure of the material produced.[8] Ophir and Wilkes reported that polyester-based polyurethanes with stronger interactions between soft and hard segments display broader transition zones than did polyether-based polymers using small angle X-ray scattering. Ng *et al.*[9] reported that materials containing a monodisperse distribution of hard segment lengths display sharper, more pronounced high temperature DSC endotherms associated with more effective packing of equilength hard blocks into microcrystalline domains. Thermal and small angle X-ray scattering studies show that the morphology of these materials is strongly influenced by aging and/or annealing.

Compositional heterogeneity in segmented polyurethanes is caused by premature phase separation.[10–12] Macosko and co-workers showed by using viscosity and turbidity measurements on a one-step polyether polyurethane in bulk that phase separation occurred when the average hard segment block length was $\fallingdotseq 1.3$. In this system, phase separation probably occurs due to segregation of longer hard segments because they become immiscible with the soft segments as their length increase or because of propensity to crystallize. Macroscopic phase separation during a two-step polymerization can be suppressed in solution using a suitable solvent. Bongston *et al.*[13] synthesized a series of polyurethanes in tetrahydrofuran. In the case of solution, single hard- and soft-segment T_g were observed, confirming the microphase nature of this system.

The morphological complexity of polyurethanes can be interpreted by taking into account the domain formation due to segregation on different levels, namely macrophase and microphase separation.

In this article, phase separation was predicted by theoretical assessment and studied for a series of polyurethanes based on 2,2-bis-[4-(2-hydroxyethoxy) phenyl]propane (BHPP) chain extender by differential scanning calorimetry and dynamic mechanical analysis.

† To whom correspondence should be addressed.

Table I. Calculated hard segment solubility δ_h, interactions per PTMG monomer unit, χ_x, and χ_{crit} for all polyurethanes

MW of PTMG	Hard segment content	MW of hard segment	No. of repeat units in the hard segment	δ_h	χ_x	χ_{crit}	$\chi_x-\chi_{crit}$	PTMG/MDI/BHPP
n	%							
2000	28	812	0.99	13.90	2.15	0.29	1.86	1:2:1
(27.77)	21	531	0.49	14.02	2.27	0.40	1.87	2:3:1
	18	436	0.32	14.10	2.36	0.46	1.90	3:4:1
1400 (19.44)	28	531	0.49	14.02	2.27	0.43	1.84	2:3:1
	23	437	0.33	14.10	2.36	0.50	1.86	3:4:1
1000 (13.88)	35	531	0.49	14.02	2.27	0.47	1.80	2:3:1
	28	390	0.24	14.15	2.41	0.59	1.82	4:5:1
650 (9.02)	45	812	0.49	14.02	2.27	0.45	1.82	2:3:1

EXPERIMENTAL

Materials

4,4′-Diphenylmethane diisocyanate (MDI, Aldrich) and poly(oxytetramethylene)glycols (PTMG, $M_n=2000$, 1400, 1000, and 650) supplied by Aldrich were dried overnight under vacuum before use. BHPP was dried under vacuum and used as received without further purification. Dimethylyacetamide (DMAc, Aldrich), was dried over 3 Å molecular seives for 5 days.

Methods

Polyurethanes were synthesized by two-step polymerization using DMAc as the solvent. All glassware was dried in an oven as 70°C overnight prior to polymerization. A typical polymerization was carried out as follows:

Dried PTMG was placed in a three-necked round-bottom flask fitted with a dry nitrogen inlet, condenser and mechanical stirrer and was heated at 70—80°C. MDI of excess 5% was added to the molten PTMG under a nitrogen. The mixture was kept for 2 h with stirring to end-cap the polyol with isocyanate. Isocyanate content of the prepolymer was determined by reacting a weighted sample with excess di-*n*-buthylamine in toluene, digested 10 min and titrated with HCl (ASTM D-1638-74). DMAc was added to the prepolymer at room temperature. A stoichiometric amount of BHPP (solution of DMAc) was added and the reaction was continued for 20 h at room temperature with mechanical stirring. Total concentration of polyurethane was 30 wt%. The polymer was precipitated in H_2O and dried under vacuum at 70°C and films were cast on the glass from a solution of polyurethanes at 70°C. This series of polyurethane ranges from a 1:2 to 4:5 equivalent ratio of PTMG to MDI at a fixed NCO/OH ratio of approximately 1.05.

DSC measurement was carried out on a Rheometric DSC instrument in the range of −120°C and 250°C at a scanning rate of 20°C min^{-1} under 20 ml min^{-1} flow of dry nitrogen as a purge gas. The second run was used for interpretation.

Dynamic mechanical measurement was done at 110 Hz using Rheovibron DDV-25FP with a heating rate of 2°C min^{-1} over a temperature range of −130°C to 150°C. Film samples of 0.4 mm thickness × 0.3 mm width × 20 mm length were prepared.

RESULTS AND DISCUSSION

Solubility Parameter

Solubility, δ, of raw material was calculated using Hoy values based on the group contribution.[14,15] Calculated δ for MDI, PTMG, and BHPP were 14.40, 9.7, and 12.9 (cal cm^{-3})$^{1/2}$ mol^{-1}, respectively.[5] Solubility parameter for MDI/BHPP hard segment varies with the molecular weight from $\delta=13.90$ to 14.15 (cal cm^{-3})$^{1/2}$ mol^{-1}. Interaction parameters, χ, can be calculated as

$$\chi=(\delta_1-\delta_2)^2 V_1/RT$$

V_1 is the molar volume of the PTMG repeat unit: 72 cm^3 mol^{-1}.

Calculated χ per PTMG unit, at room temperature, for different PTMG hard segment combinations are in Table I. χ of about 2 show that soft and hard segment are incompatible at room temperature.

For two polymers of infinite molecular length to mix, χ must be zero or negative. In the case of mixing of two blocks, the critical value for the phase separation is dependent on block size:

$$\chi_{crit}=0.5[(1/x_A)^{1/2}+(1/x_B)^{1/2}]^2$$

where x_A and x_B are degrees of polymerization of component A and B. x_A were taken to be $2n+1$, where n is the number of repeating units in the hard segment, and 1 for the terminating MDI unit of each hard segment. Thus x_A for the hard segment consisting of MDI-BHPP-MDI units is 3, and $n=1$.

In general, with increasing χ, miscibility of two polymer decreases, easily leading to phase separation.

Blocks should be miscible if χ_{crit} is greater than χ at

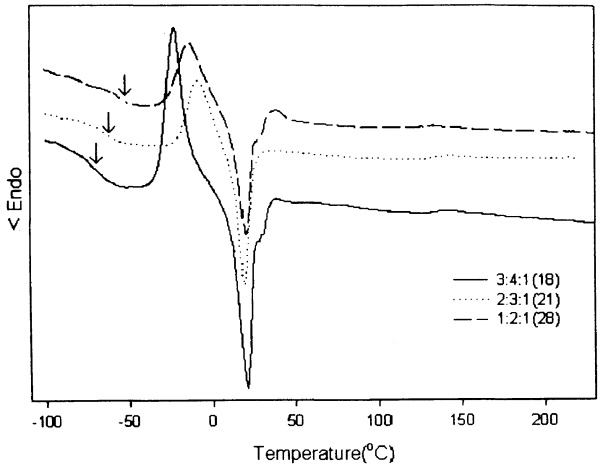


Figure 1. DSC thermograms of polyurethanes with PTMG 2000.

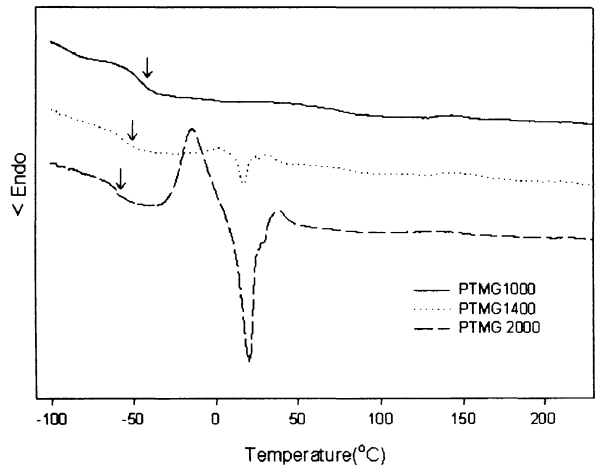


Figure 2. DSC thermograms of polyurethanes with the same hard segment content (28%).

the given temperature. As the molecular weight of soft segment increases, χ of hard and soft segment increases, giving less miscibility. Thus, the degree of phase separation increases and T_g of soft segment decreases. Calculated χ_{crit} for all polyurethanes are given in Table I.

Table I shows the values of interactions as well as number of repeat units n in the hard segment. Comparison of χ with corresponding χ_{crit} shows that hard and soft segment are immiscible in all polymers. It seems that crystalline PTMG mixes less readily with the hard segment. The difference between χ_x and χ_{crit} decrease with the increase of the hard segment content and the increase of molecular weight of the soft segment. This analysis is approximate, since it does not take into account several important factors. First, the effect of connectivity of the two segments is not known, but lowering the entropy of mixing is expected. Also, all considerations based on the Flory–Huggins theory of polymer solution assume that there are no interactions between the two components, which is not true here.

Differential Scanning Calorimetry

DSC thermograms of the polyurethanes based on PTMG 2000 with different hard segment contents are represented in Figure 1. The soft segment glass transition is well defined around $-60°C$. All samples clearly show the soft segment cold crystallization and soft segment melting but not melting of hard segments. Crystallinity in the soft segment results from the highly regular and symmetrical PTMG with higher molecular weight, suggesting high immiscibility between hard and soft segment and rapid crystallizability of PTMG.[16] These samples have very high soft segment content, more than 72 wt%. This behavior was observed in dynamic mechanical analysis.

T_g of soft segment increases with hard segment content. Such deviation of T_g and broad transition are generally considered to result from partial mixing between hard and soft segment and restriction of rotation of the soft segment linked to the hard domain.[3,5,6,16] This supports the intuitive view that as the hard segment content increases, phase mixing increases. This may be expected by comparing difference between χ_x and χ_{crit}. Generally speaking, this observation is in agreement with the studies by Petrovic.[5]

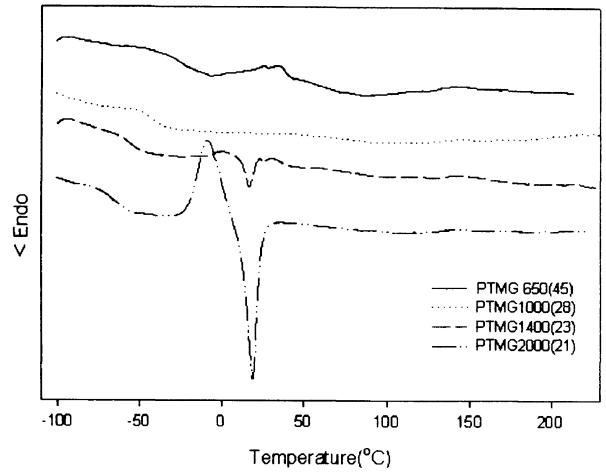


Figure 3. DSC thermograms of polyurethanes with different M_n of PTMG at fixed molar ratio (PTMG : MDI : BHPP = 2 : 3 : 1).

The same was found for the other polyurethanes, synthesized with different PTMG. There is no crystallinity for the polyurethanes made from a soft segment of MW ≤ 1400. The effects of soft segment chain length on the thermal behavior were investigated varying the soft segment molecular weight from 1000 to 2000 at a fixed hard segment content (28 wt%). The results are shown in Figure 2.

The glass transition temperature of the soft segments increases with decreasing molecular weight of the soft segments. The thermal behavior in the polyurethanes with the same composition (PTMG : MDI : BHPP = 2 : 3 : 1) was found similar (Figure 3).

The effects of hard segment on T_g of soft segment is much stronger with shorter polyol which could be ascribed to hydrogen bonding. Hard segments restrict the freedom of rotation of the soft segment. The restrictions become more pronounced when PTMG is linked to the blocks.

Polyurethane based on PTMG 650 with hard segment content 45 wt% had a broad endotherm of hard segment. This endotherm from 50°C to 100°C was assigned to the change of aggregation of hard segment. Polyurethane with hard segment content above 35% had detectable crystalline regions by DSC.[17,18] But all samples did not

Table II. Quantitative DSC evaluation of the degree of phase separation of the soft segment

MW of PTMG	Hard segment content/%	T_g of soft segment (onset)/°C	ΔC_p	$\Delta C_p/\Delta C_{po}$
2000	28	−56 (−65)	0.23	0.63
	21	−65 (−72)	0.31	0.86
	18	−68 (−75)	0.35	0.97
1400	28	−54 (−60)	0.23	0.63
	23	−55 (−62)	0.34	0.94
1000	35	−42 (−51)	0.24	0.66
	28	−45 (−55)	0.29	0.80
650	45	−22 (−36)	0.34	0.60

show clear melting endotherms of the hard segment. It is likely that chain extender BHPP inhibits aggregation of hard segment through hydrogen bond. This may be due to weak effective attraction and steric hindrance of BHPP with long chain.

All polyurethanes containing BHPP have lower T_g of soft segment than that of other chain extender used polyurethanes,[7,8,17] suggesting high phase separation compared to polyurethanes based on other chain extender. A possible explanation of this behavior is that hard segments containing BHPP have relatively flexible character and weak attractive interaction, which less restrict the motion of the segments of soft domain.

Through an analysis of the shift broadening and heat capacity, ΔC_p, of the T_g of the soft blocks, qualitative and also quantitative assessment can be found for the compositions of the phases and interfacial area. The underlying idea in this methods is that ΔC_p at T_g is proportional to the mass of the polymer chains taking part in the transition. Soft segments dissolved in the hard phase are not expected to contribute to ΔC_p, since their mobility is restricted. Thus, the degree of phase mixing can be represented as,

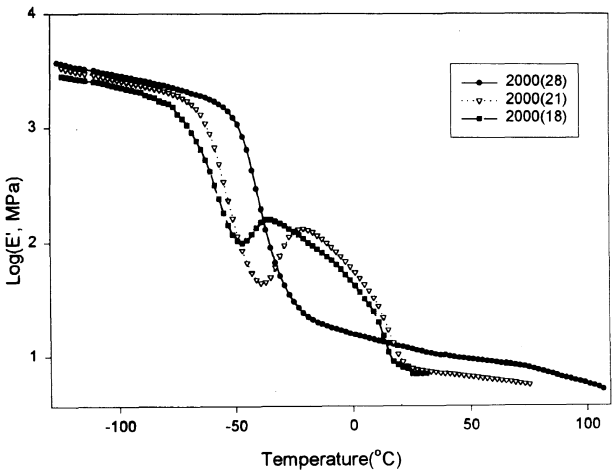
$$\Delta C_p(T_g)/\Delta C_{po}(T_g)$$

where ΔC_p refers to the segmented polymer and ΔC_{po} to the reference (pure soft segment). The assumption is made that ΔC_p of the hard phase in the region of measurement is negligible. $\Delta C_p/\Delta C_{po}$ corresponds to the percent of segregation of the soft blocks.[6,7]

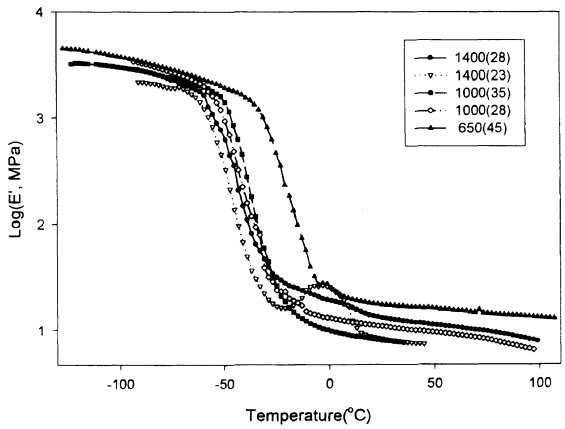
The ratios for all polyurethanes are given in Table II. That clearly demonstrated the phase segregation ratios to decrease with increasing hard segment content.

But no clear effect of soft segment molecular weight is seen. Although it is clear from T_g shift that the sample with PTMG 650 shows a certain degree of mixing, no significant difference between series is observed by the heat capacity change (ΔC_p).[19−21] In this case, the theoretical consideration based on heat capacity change is inadequate.

The polyurethanes made from lower molecular weight PTMG and higher hard segment content have more miscibility between the hard and soft segments. The more hard segments are dispersed in the soft segments, the more restrictive are the soft segments. Evidence to support this is seen in the dynamic mechanical results.



(a) Polyurethanes based on PTMG 2000

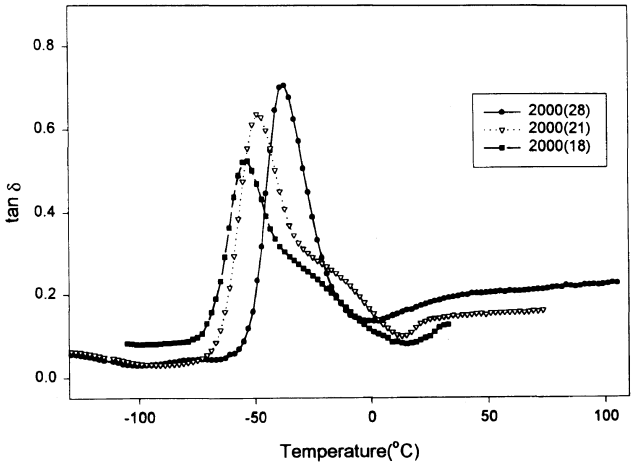


(b) Polyurethanes based on PTMG 1400, 1000, and 650

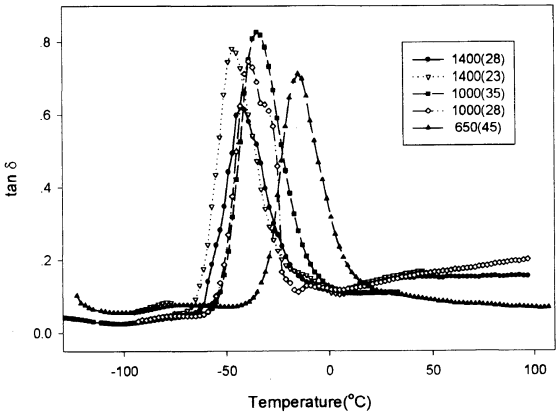
Figure 4. Storage modulus as function of temperature of polyurethanes.

Dynamic Mechanical Analysis

The storage modulus (E') of the investigated polyurethanes are given in Figure 4. Both series of samples exhibit a major relaxation (β relaxation) and one rubbery plateau corresponding to the two phase in the material. This is characterized by significant decrease in the storage modulus, which corresponds to the glass transition temperature of the soft segments.[3,22] For all samples, T_g of the soft phase was a little difficult to identify using DSC. It should be noted the DMA technique generally provides higher T_g values than dose DSC (usually up to 10°C higher) due to the dynamic nature of the test.[8] As hard segment content increases, enhanced rubbery modulus is observed. This is due to increase in the size and inter-connectivity of the hard segment domains as the sample has more hard segment content. The shift of transition regions to higher temperature with increasing hard segment length can be attributed to the greater fraction of hard segments dissolved in the soft phase, indicating partial phase mixing between the hard and soft segment. This is well



(a) Polyurethanes based on PTMG 2000



(b) Polyurethanes based on PTMG 1400, 1000, and 650

Figure 5. tan δ as function of temperature of polyurethanes.

in accord with the results of DSC.[4,18,23,24]

Soft segment crystallinity is observed in samples with high soft segment content. The depression and subsequent elevation of the modulus above T_g are assigned to the crystallization of the soft segment.

The temperature dependence of tan δ from the mechanical measurement is given in Figure 5. That illustrates loss peaks associated with glass transition and damping capacity of soft domains.[25-27] The sharpness and height of the damping peaks give information about the degree of order and the freedom of motion of molecules in the soft domains. All samples display the most prominent damping peaks, suggesting that they are all nearly amorphous.[28,29]

The positions of damping peaks provide information about the degree of phase separation.[8]

More phase separation can be expected as soft segment molecular weight increases. The peaks of β relaxation shift to higher temperature as the hard segment content increases and molecular weight of PTMG decreases. The difference between the peaks of β relaxation of the soft segment is indication of the relative number of hard blocks dissolved in the soft phase, suggesting the degree of phase mixing.

Soft segment crystallization can be further described by the shape of the tan δ peak.[16] tan δ peak of the sample with high soft segment content becomes lower and broader as the degree of the soft segment crystallinity in the soft segment increases. A second relaxation around $-20°C$ was observed in these samples as a shoulder of the tan δ peak.

CONCLUSION

Microphase-separated polyurethanes based on MDI, PTMG, and 2,2-bis-[4-(2-hydroxyethoxy)phenyl]propane were synthesized by two-step solution polymerization and thermal and phase separation behavior was studied. The extent of phase separation was determined by the heat capacity change, ΔC_p, at the glass transition temperature of the soft segment. From the DSC and DMA investigation, molecular weight of the soft segment and hard segment content were found to have influence on the glass transition. Polyurethanes based on PTMG 2000 have endotherms of soft segment melting, which means immiscibility between hard and soft segment. But there is no crystallinity for the polyurethane made from soft segment of MW ≤ 1400. With decreasing molecular weight of soft segment, the glass transition temperature increases. With increasing hard segment content, glass transition temperature increases, indicating the restriction of freedom of soft segment rotation. The difference of the glass transition for the pure soft and soft segments of polyurethane is indication of the partial phase mixing. Polyurethanes made from lower molecular weight PTMG and higher hard segment content may thus have more phase mixing between hard and soft segments.

Polyurethanes based on BHPP have lower T_g of soft segment than that of ordinary chain extender used ones due to the flexible hard segment with weak attractive interaction.

REFERENCES

1. H. D. Kim, J. H. Huh, E. Y. Kim, and C. C. Park, *J. Appl. Polym. Sci.*, **69**, 1349 (1998).
2. A. G. Parthiraja, F. M. Gordon, R. Ezio, C. C. Ronald, J. M. Simon, B. Arhtur, and S. Klaus, *J. Appl. Polym. Sci.*, **46**, 319 (1992).
3. R. F. Harris, M. D. Joseph, C. Davidson, C. D. Deporter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 509 (1989).
4. C. M. Brunette, S. L. Hsu, M. Rossman, W. J. MacKnight, and N. S. Schneider, *Polym. Eng. Sci.*, **21**, 668 (1981).
5. Z. S. Petrovic, *J. Polym. Sci. Polym. Phys.*, **27**, 545 (1989).
6. L. Cuve, J.-P. Pascault, G. Boiteux, and G. Seytre, *Polymer*, **32**, 343 (1991).
7. L. Cuve and J.-P. Pascault, *Polymer*, **33**, 3957 (1992).
8. J. M. Darren, F. M. Gordon, M. R. Gordon, A. Pathiraja, Gunatillake, and J. M. Simon, *J. Appl. Polym. Sci.*, **60**, 557 (1996).
9. H. N. Ng, A. E. Allegrezza, F. W. Seymour, and S. L. Cooper, *Polymer*, **14**, 255 (1973).
10. J. M. Castro, F. Lopez-Serrano, R. E. Carmargo, C. W. Macosko, and M. V. Tirrell, *J. Appl. Polym. Sci.*, **26**, 2067 (1981).
11. J. M. Castro, C. W. Macosko, and S. J. Perry, *J. Polym. Commun.*, **25**, 83 (1984).
12. R. E. Camargo, C. W. Macosko, M. V. Tirrell, and S. T. Wellinghoff, *Polym. Eng. Sci.*, **22**, 719 (1982).
13. B. Bengston, C. Feger, and W. J. MacKnight, *Polymer*, **26**, 895 (1985).
14. D. R. Paul and S. Newman, Ed, "Polymer Blends," Vol. 1, Academic Press, New York, N.Y., 1978.
15. D. W. Van Krevelen and P. J. Hoftyzer, "Properties of Polymer–Correlations with Chemical Structure," Elsevier, Amsterdam, 1972, p 85.
16. W.-P. Chen, K. C. Frisch, D. J. Kenney, and S. W. Wong, *J.*

Macro. Sci., **A29**, 567 (1992).
17. J. A. Miller, S. B. Lin, K. K. S. Hwang, K. S. Wu, P. E. Gibson, and S. L. Cooper, *Macromolecules*, **18**, 32 (1985).
18. C. J. Paul and M. R. G. Nair, *Polym. Eng. Sci.*, **38**, 440 (1998).
19. L. Cuve, J.-P. Pascault, G. Boiteux, and G. Seytre, *Polymer*, **32**, 343 (1991).
20. J. W. C. Van Bogart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 65 (1983).
21. Y. Camberlin and Pascault, *J. Polym. Sci. Chem.*, **21**, 415 (1983).
22. R. F. Harris, M. D. Joseph, C. Davidson, C. D. Deporter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 487 (1990).
23. T. Murayama, "Dynamic Mechanical Analysis of Polymeric Materials," Elsevier, New York, N.Y., 1978.
24. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, London, 1967.
25. X. He, X. Jia, and X. Yu, *J. Appl. Polym. Sci.*, **54**, 207 (1994).
26. P. J. Stenhouse, E. M. Valles, S. W. Kantor, and W. J. MacKnight, *Macromolecules*, **22**, 1467 (1989).
27. A. F. Yee and S. A. Smith, *Macromolecules*, **14**, 54 (1981).
28. G. L. Wikes and R. Wildnaur, *J. Appl. Phys.*, **46**, 4148 (1975).
29. G. A. Senich and W. J. MacKnight, *Adv. Chem. Ser.*, No. 176 (1979).