Degree of phase separation in polyether–polyurethane copolymers with different chemical structures of hard segments

Jin-Long Hong*
Institute of Materials Science and Engineering, National Sun-Yat Sen University, Kaohsiung, Taiwan 80424, R.O.C.

and C. Peter Lillya and James C. W. Chien
Department of Chemistry, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA
(Received 22 August 1991; revised 29 November 1991; accepted 16 December 1991)

Polyether–polyurethane (PEPU) copolymers based on poly(propylene glycol) (PPO), 4,4'-diphenylmethane diisocyanate (MDI), and different chain extenders [1,5-pentanediol (P), diethylene glycol (D), triethylene glycol (T), and 1,3-bis(*N*,*N*'-methyl-*N*,*N*'-2-hydroxyethyl)isophthalamide (Bi(M))] were prepared and characterized. The gross properties and the carbonyl absorption patterns in i.r. spectroscopy suggest that the degree of phase separation or hard domain crystallinity decreases in the order of P- > D- > Bi(M)- and T-extended PEPU. D.s.c. results suggest phase-separated systems of PPO/MDI/P, PPO/MDI/D and PPO/MDI/Bi(M), in contrast to a phase-mixed PPO/MDI/T system. The absence of a high temperature melting transition refers to the existence of an amorphous hard domain in the PPO/MDI/Bi(M) system. Chain length, flexibility, and aromatic content of the applied chain extenders control the extent of phase separation of the final products.

(Keywords: polyether–polyurethane; degree of phase separation; hard segment content; chemical structures; chain extender)

INTRODUCTION

The unusual properties of segmented $(AB)_n$ copolymers are directly related to their two-phase microstructure[1]. Urethane copolymers are one of the species with the interesting structure of alternating blocks and possess the phase-separated hard-segment-rich domain interconnected by the soft-segment-rich matrix[2–7]. The perfection and degree of phase separation have been found to be important to the strength and the high elasticity of the final polymers. Also, besides the frequently discussed effects from thermal history[8–11], factors governing phase separation are directly related to synthesis pathways and the chemical compositions. Usually, urethane segmented copolymers are synthesized by a two-step condensation process[12–14]. The reaction components consist of a bifunctional soft polydiol, the basic hard segment component (a diisocyanate), and a chain extender as the constructing element for the hard segment. Phase separation is related to the dissimilarity between hard and soft segment; the degree of phase separation can therefore be manipulated by changing the chemical compositions of the soft polydiol and chain extender.

Polyether–polyurethane (PEPU) copolymers of the 4,4'-diphenylmethane diisocyanate/1,4-butanediol (MDI/BD) system and their properties in relation to hard segment content[15,16], length and distribution[17,18] have been studied extensively. Despite a large number of investigations on PEPU, studies on the relationship between chemical structure of the hard segment and phase separation behaviour are scarce. Accordingly, use of chain extenders with different chain length, flexibility, steric bulkiness and aromatic content is attempted in this study to provide PEPU with different chemical structures of hard segment and to disclose the critical role of hard segment on degree of phase separation.

EXPERIMENTAL

Materials and instrumentation

All reagents and solvents were of reagent grade. Argon was purified by passing through a BTS column and drying with NaOH. Triethylene glycol (Aldrich, 99%) was predried with $CaSO_4$ for 1 week before vacuum distillation and was stored under argon. Diethylene glycol (D; Aldrich, 99%) and 1,5-pentanediol (P; Aldrich, 99%) were distilled from CaH_2 and stored under argon. 4,4'-Diphenylmethane diisocyanate (MDI; Mobay) was vacuum distilled and stored in a refrigerator before use. Poly(propylene glycol) (PPO) diol, $M_n = 2000$ (Polyscience) and *N*,*N*-dimethylformamide (DMF; Fisher Scientific, Spectroanalyzed) were stored under argon and over molecular sieve 3 Å (Fisher). Dimethyl

---

*To whom correspondence should be addressed

0032-3861/92/204347-05

isophthalate (Aldrich, 99%) was used without further purification.

I.r. spectra were recorded by a Perkin-Elmer model 1420 ratio recording i.r. spectrometer, using solvent-cast film on sodium chloride discs. Thermal transition temperatures were determined using a Perkin-Elmer DSC-2 differential scanning calorimeter connected to the thermal analysis data station.

Synthesis of polyether–polyurethane segmented block copolymers

1,3-Bis(*N*,*N*′-methyl-*N*,*N*′-2-hydroxyethyl) isophthalamide (Bi(M)) was synthesized by aminolysis of the dimethyl isophthalate with *N*-methylaminoethanol[19]; elemental analysis indicated: C, 59.70 (60.00, theoretical); H, 7.34 (7.10); N, 9.74 (10.00). A two-step solution process was used for the synthesis of PEPU copolymers. Reactions were carried out in a three-necked round-bottom flask equipped with a mechanical stirrer and argon inlet and outlet tubes. Various amounts of PPO and MDI were stirred vigorously and heated to 60–70°C before addition of 5 wt% dibutyltin dilaurate. Reaction was allowed to proceed for 1 h and the reaction mixture was then cooled to room temperature. *N*,*N*-Dimethylformamide (DMF) was then added in such a way that the amount of DMF in millilitres was equal to twice the total weight of reactants in grams. Liquid chain extenders were directly introduced whereas solid Bi(M) was added as DMF solution. The second step, chain extension, was run for 4 h and monitored with i.r. spectroscopy by following the gradual disappearance of the isocyanate band at 2270 cm^{-1}. A small amount of methanol was used to quench the reaction. The polymer solution (30–50% by weight) was poured onto sheets of Teflon-coated poly(vinyl chloride) or dropped onto sodium chloride discs (for i.r. analysis). Solvent was allowed to evaporate for a period of 2 days. The resulting sample was further dried in a vacuum oven ($\sim$0.13 kPa) at 80°C for 2 days.

RESULTS AND DISCUSSION

Preliminary investigation

Details of the PEPU copolymers and their gross physical properties are summarized in *Table 1*. As hard segment content of PEPU copolymers increases, the polymers become harder and eventually become stiff materials. A previous study[16] showed that a dramatic change in the tensile properties of PEPU based on poly(oxypropylene-oxyethylene)diol/MDI/BD occurs at about 60 wt% hard segment content, the phase inversion point. In our study, samples of 1/10/9(PPO/MDI/P)-63 wt% and 1/10/9(PPO/MDI/D)-63 wt% were hard materials and could not be stretched by hand, and should therefore lie in the vicinity of the phase inversion point. For accurate determination of the phase inversion point, however, samples with extended range of hard segment content would be needed.

The PPO/MDI/T system generally showed inferior mechanical properties as compared to other systems in the present study. The viscous and gummy appearance suggests much limited demixing in this system. The long and flexible triethylene ether chain possibly inhibits the crystallization of hard segment and enhances the hard–soft phase mixing for the corresponding PEPU copolymer as supported by our d.s.c. results in the following section.

I.r. spectroscopy

In the urethane hard domain, hydrogen bonds result from the interactions of hydrogen atoms of NH groups and the carbonyl groups. In a PEPU copolymer, the NH groups form hydrogen bonds with the C=O groups of the urethane linkages as well as the soft segment oxygen atoms due to the possible hard–soft phase interactions. *Figure 1* shows the i.r. spectra of selected PEPU copolymers in the NH and C=O absorption regions. Absorption of non-bonded NH groups (3500–3600 cm^{-1}) appears as a shoulder to bonded NH absorption (centred at 3320 cm^{-1}). Non-bonded carbonyls are centred in the range 1740–1723 cm^{-1}, while bonded carbonyls are centred in the range 1714–1700 cm^{-1}. Assuming an equal sample thickness for all the test samples, *Figure 1* shows that the fraction of bonded carbonyl absorption increases with increasing hard segment content, from 1/3/2(PPO/MDI/P) to 1/5/4 (PPO/MDI/P) and from 1/3/2(PPO/MDI/D) to 1/5/4(PPO/MDI/D). Similar observations have been made for the poly(tetramethylene oxide)/MDI/BD system[20]. The average hard domain size and therefore

Table 1 Preliminary evaluation of sample properties of all PEPU copolymers

PEPU polymer[a] (wt% of hard segment)[b]	Product properties	PEPU polymer[a] (wt% of hard segment)[b]	Product properties
1/10/9(PPO/MDI/P) (63)	Stiff material[c]	1/5/4(PPO/MDI/Bi(M)) (54)	Strong elastomer[d]
1/5/4(PPO/MDI/P) (45)	Strong elastomer[d]	1/4/3(PPO/MDI/Bi(M)) (48)	Elastomer[e]
1/3/2(PPO/MDI/P) (32)	Elastomer[e]	1/3/2(PPO/MDI/Bi(M)) (39)	Elastomer[e]
1/2/1(PPO/MDI/P) (23)	Gummy material	1/2/1(PPO/MDI/Bi(M)) (28)	Gummy material
1/10/9(PPO/MDI/D) (63)	Stiff material[c]	1/3/2(PPO/MDI/T) (34)	Gummy material
1/5/4(PPO/MDI/D) (45)	Strong elastomer[d]	2/5/3(PPO/MDI/T) (29)	Gummy material
1/3/2(PPO/MDI/D) (32)	Elastomer[e]	1/2/1(PPO/MDI/T) (24)	Viscous liquid
1/2/1(PPO/MDI/D) (23)	Gummy material		

[a] A shorthand system of X/Y/Z(PPO/MDI/chain extender) was used to identify all the PEPU copolymers, where X/Y/Z refers to the mole ratios of PPO, MDI and the applied chain extenders (P, D, T and Bi(M))

[b] Hard segment content (%) = $(A/A + B) \times 100\%$, where A = wt of MDI + wt of chain extender and B = wt of soft polydiol used in the synthesis step

[c] Can be bent but cannot be stretched

[d] Can be stretched with difficulty

[e] Can be stretched easily by hand

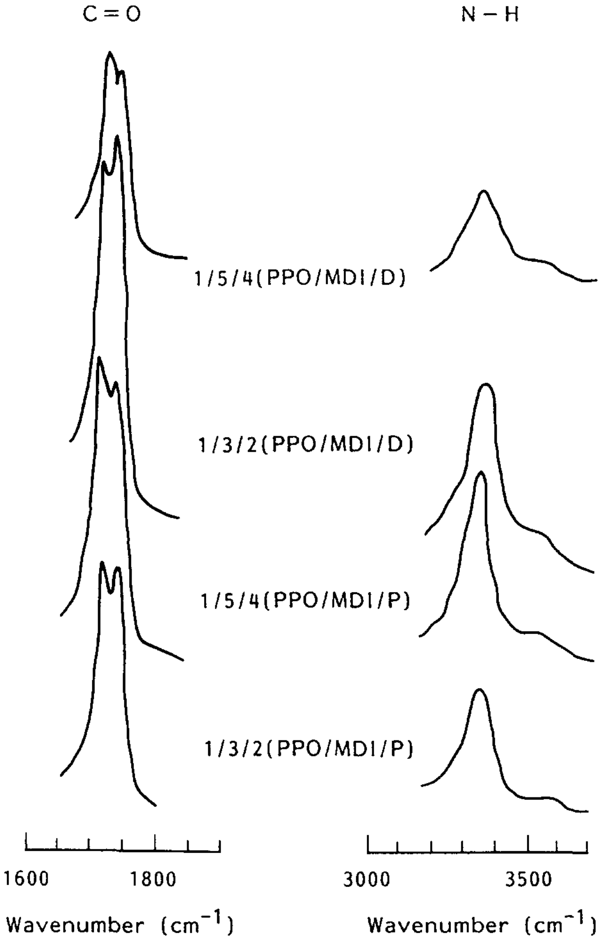

Figure 1 I.r. spectra of PEPU copolymers, carbonyl and –NH region: effect of hard segment content

the extent of interurethane interactions are suggested to increase with the hard segment content.

Spectra of PEPU copolymers with different hard segments are compared in *Figure 2*. The carbonyl absorption band splits into two peaks, hydrogen-bonded (1714–1700 cm^{-1}) and free (1740–1723 cm^{-1}) carbonyl absorptions. Qualitative comparisons of the two carbonyl bands indicate that 1/3/2(PPO/MDI/P) has more bonded carbonyl than 1/3/2(PPO/MDI/D). Previous results[21] revealed that the interurethane bonded carbonyl groups (NH····O=C) generally reside in the interior of hard domain, whereas the hard segments possessing free carbonyl groups are present in the mixed soft phase or at the interface. Therefore, a higher degree of phase mixing is indicated in sample 1/3/2(PPO/MDI/D) than in sample 1/3/2(PPO/MDI/P).

In contrast, 1/3/2(PPO/MDI/T) and 1/3/2(PPO/MDI/Bi(M)) exhibit one broad carbonyl absorption. This broad absorption is probably the result of superposition of many absorption bands corresponding to a range of N–H····O hydrogen bond distances. Hwang *et al.*[22] observed these different types of carbonyl absorptions in PEPU polymers. They suggested that in a perfect crystal urethane segments possessing a constant hydrogen bond distance should exhibit sharp and narrow NH and carbonyl absorption peaks, in contrast to the rather broad peaks of the same material in an amorphous phase. Thus, our absorptions can be interpreted in two different ways. First, amorphous or highly disordered hard domains could cause this broad carbonyl absorption. Second, a high degree of phase mixing might prevent hard segment from forming hard domain of regular structure, and therefore any regular interaction pattern between urethane carbonyls and NH groups. The physical properties of T-extended PEPU show that no true hard phase is present, in agreement with their featureless carbonyl bands.

Differential scanning calorimetry

The influence of hard segment content on the glass transition of soft segment (T_{sg}) can be used to indicate the degree of phase separation in PEPU. Schneider *et al.*[5] have attributed the increase of T_{sg} with increasing hard segment content to a combination of the copolymer effect and effective crosslinking of soft block oxygens by hydrogen bonding with urethane NH groups. Generally, a relatively constant value of T_{sg} with increasing hard segment content is observed in a phase-separated system. As shown in *Table 2*, the glass transition temperature of PEPU copolymers, except those in the PPO/MDI/T system, is relatively constant despite the increase of hard segment content.

The interrelation between i.r. and d.s.c. results is now discussed. I.r. and d.s.c. analyses disclosed that P- and D-extended PEPU copolymers possess both a high degree of phase separation and crystalline hard domains.

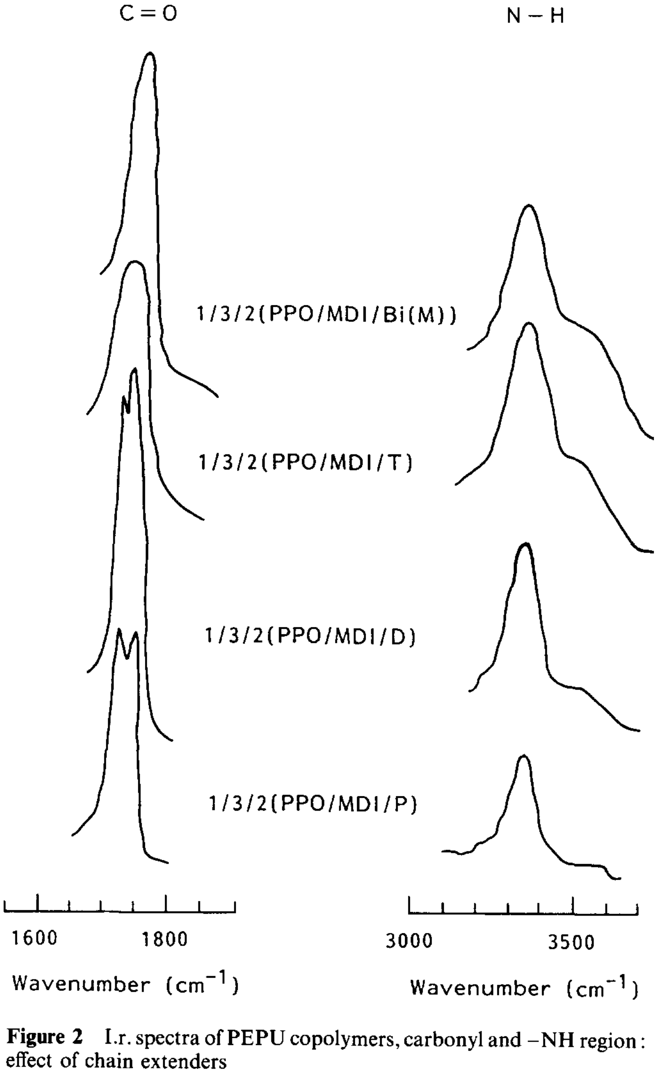

Figure 2 I.r. spectra of PEPU copolymers, carbonyl and –NH region: effect of chain extenders

Table 2 D.s.c. analysis of PEPU copolymers

Sample	Hard block (wt%)	T_{sg}[a] (°C)	T_{hg}[b] (°C)	T_m (°C)
1/10/9(PPO/MDI/P)	63	–	83	174[c]
1/5/4(PPO/MDI/P)	45	−44	84	171[c]
1/3/2(PPO/MDI/P)	32	−47	89	156[c]
1/10/9(PPO/MDI/D)	63	–	81	175[c]
1/5/4(PPO/MDI/D)	45	−45	83	163[c]
1/3/2(PPO/MDI/D)	32	−44	83	145[c]
1/5/4(PPO/MDI/Bi(M))	54	−50	57	200[d]
1/3/2(PPO/MDI/Bi(M))	39	−50	57	157[d]
1/2/1(PPO/MDI/Bi(M))	28	−50	–	135[d]
1/3/2(PPO/MDI/T)	34	−37	52	132[d]
2/5/3(PPO/MDI/T)	29	−41	55	–[d]
1/2/1(PPO/MDI/T)	24	−43	47	130[d]

[a] Glass transition temperature of soft segment, onset temperature

[b] Secondary transition temperature due to dissociation of hard–soft interaction in the interlayer of hard domain boundary, onset temperature

[c] Melting transition temperature, peak maximum

[d] Decomposition multiple peak observed during polymer melting, peak maximum

In contrast, T-extended PEPU are viscous liquids, presumably owing to extensive phase mixing. The Bi(M)-extended polymers provide ambiguous results. These are typically soft elastomers and thus probably phase separated. In fact, T_{sg} is independent of hard segment content, consistent with a high degree of phase separation. Yet the carbonyl band in the i.r. is broad, indicative of disordered hard domains. It appears that the lower hydrogen-bond density and steric hindrance introduced by the *N*-methyl groups are more important than the stacking tendency for the aromatic rings of Bi(M) units and thus disordered hard domains result. Nevertheless, owing to the presence of aromatic rings in the hard segments, phase separation is maintained.

Unambiguous evaluation of melting temperatures for PEPU was complicated by thermal decomposition during d.s.c. scans. Evidence for decomposition in the form of multiple endothermic peaks were observed for all PEPU copolymers except P- and D-extended PEPU. Selected d.s.c. thermograms of PEPU with 1/5/4 composition are given in *Figure 3*. Multiple endothermic peaks for 1/5/4(PPO/MDI/Bi(M)) were not observed on the second heating after quenching samples from 220°C. Also, the generation of viscous liquid after d.s.c. scans refers to the occurrence of decomposition during heating. In contrast, the melting peaks in thermograms of 1/5/4(PPO/MDI/P) and 1/5/4(PPO/MDI/D) can be regenerated on the second scans. This suggests the existence of crystalline hard domain, while the absence of melting transition before decomposition implies that domains in Bi(M)-extended PEPU are amorphous.

The inherent chemical structures of the applied chain extenders play an important role in determining the final properties of PEPU copolymers. First, regarding the flexibility of the chain extender, triethylene glycol (T), with its long chain and high content of flexible ether bonds, should have the highest flexibility of the chain extenders used here. The flexibility of the triethylene moiety results in the substantial phase mixing in the derived PEPU. Diethylene glycol (D), with two flexible C–O linkages in replacing the central C–C bonds of 1,5-pentanediol (P), should have higher flexibility than pentanediol. This explains the higher degree of phase separation in P- than D-extended PEPU. Second, chain extenders with a higher density of aromatic rings will exhibit a higher degree of phase separation due to the large difference of the solubility parameter between hard segment of high aromaticity and soft segment of purely aliphatic chain. This results in a phase-separated PPO/MDI/Bi(M) system. Nevertheless, the steric bulkiness of aromatic ring and *N*-methyl groups in Bi(M) may inhibit the formation of well packed crystalline hard domain.

CONCLUSIONS

Four series of PEPU copolymers based on 1,5-pentanediol (P), diethylene glycol (D), triethylene glycol (T), and 1,3-bis(*N*,*N'*-methyl-*N*,*N'*-2-hydroxyethyl)isophthalamide (Bi(M)) as chain extenders were synthesized and characterized. By changing the composition of the blocks, the resulting polymers can vary from liquids to solids, which can be either elastomeric or plastic in nature. Also, variation of the applied chain extenders changes many molecular properties such as polarity, hydrogen-bonding capability, and crystallinity of the blocks.

I.r. absorptions of urethane, –NH and carbonyl groups appear as separate free and hydrogen-bonded peaks which give preliminary information about the crystallinity of hard domains or the degree of phase separation. Differences in pattern and intensity between free and bonded carbonyl absorptions indicate that the degree of phase separation or hard domain crystallinity decreases in the order P- > D- > Bi(M)- and T-extended polymers. D.s.c. studies of the thermal transitions of these

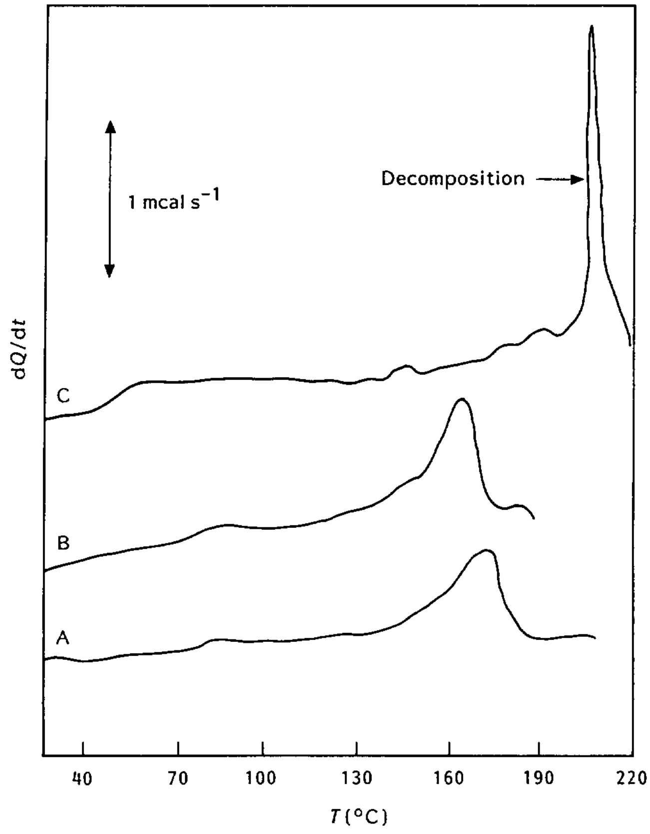

Figure 3 High temperature d.s.c. thermograms of selected PEPU with 1/5/4 composition: A, 1/5/4(PPO/MDI/P); B, 1/5/4 (PPO/MDI/D); C, 1/5/4(PPO/MDI/Bi(M))

PEPU polymers give results consistent with i.r. observations. The glass transition temperatures of the soft segments (T_{sg}) remain relatively intact with increasing hard segment content in systems PPO/MDI/P, PPO/MDI/D and PPO/MDI/Bi(M). The increase of T_{sg} with hard segment content for PPO/MDI/T suggests a high degree of phase mixing in these polymers; the gummy or liquid appearance of these polymers, as well as i.r. spectra, are in accord with such a mixing of hard and soft segments. The broad carbonyl absorption in the i.r. spectra and the constant T_{sg} with increasing hard segment content imply the existence of amorphous hard domain in Bi(M)-extended PEPU. This is also demonstrated by the absence of melting transition in Bi(M)-extended PEPU.

REFERENCES

1 Van Bogart, J. W. C., Lilaonitkul, A. and Cooper, S. L. in 'Multiphase Polymers', Advances in Chemistry Series 176 (Eds S. L. Cooper and G. M. Estes), American Chemical Society, Washington, DC, 1979, p. 3

2 Schollenberger, C. S. and Dinbergs, K. *J. Elastomers Plast.* 1975, **7**, 65

3 Samuels, S. L. and Wilkes, G. L. *J. Polym. Sci.* 1973, **C43**, 149

4 Chang, Y. and Wilkes, G. L. *J. Polym. Sci.* 1975, **13**, 455

5 Schneider, N. S., Paik Sung, C. S., Matton, R. W. and Illinger, J. *Macromolecules* 1975, **8**, 62

6 Bonart, R., Morbitzer, L. and Rinke, H. *Kolloid-Z. Z. Polym.* 1970, **240**, 807

7 Cooper, S. L. and Tobolsky, A. *J. Appl. Polym. Sci.* 1966, **10**, 1837

8 Seymour, R. W. and Cooper, S. L. *Macromolecules* 1973, **6**, 48

9 Wilkes, G. L. and Emerson, J. A. *J. Appl. Phys.* 1976, **47**, 4261

10 Lee, H. S., Wang, Y. K. and Hsu, S. L. *Macromolecules* 1987, **20**, 2089

11 Abouzar, S. and Wilkes, G. L. *J. Appl. Polym. Sci.* 1984, **29**, 2695

12 Allport, D. C. in 'Block Copolymers' (Ed. W. H. James), Wiley, New York, 1973, p. 234

13 Noshay, A. in 'Block Copolymers, Overview and Critical Survey' (Ed. J. E. McGrath), Academic, New York, 1977, p. 367

14 Ultrich, H. *J. Polym. Sci., Macromolecular Rev.* 1976, **11**, 93

15 Seefried, C. G. Jr, Koleske, J. V. and Critchfield, F. E. *J. Appl. Polym. Sci.* 1975, **19**, 2503

16 Zdrahala, R. J., Gorkin, R. M., Hager, S. L. and Critchfield, F. E. *J. Appl. Polym. Sci.* 1979, **24**, 2041

17 Blackwell, J., Nagarajian, M. R. and Hoitink, T. B. *Polymer* 1982, **23**, 950

18 Miller, J. A., Hwang, K. K. S., Gibson, P. E., Cooper, S. L., Lin, S. B. and Wu, K. S. *Macromolecules* 1985, **18**, 32

19 Xu, B., Khanna, D. N., Lillya, C. P. and Chien, J. C. W. *J. Appl. Polym. Sci.* 1986, **31**, 123

20 Lin, S. B., Hwang, S. Y., Tsay, S. Y. and Cooper, S. L. *Colloid Polym. Sci.* 1985, **263**, 128

21 Cooper, S. L., West, J. C. and Seymour, R. W. 'Encyclopedia of Polymer Science and Technology' (Eds H. F. Mark and N. M. Bikales), Wiley, New York, 1976, Suppl. 1, p. 521

22 Hwang, K. K. S., Wu, G., Lin, S. B. and Cooper, S. L. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 1677