Interstitial polymers based on a polyurethane network:
1. Melting points and fractional crystallinities

I. Aladesulu*, N. B. Graham and R. W. Richards†
Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, UK
(Received 22 March 1982)

The preparation of a series of interstitial polymers based on a polyurethane network is described, the 'guest' polymers being poly(methyl acrylate) and poly(methacrylic acid). Differential scanning calorimetry has been used to determine the melting points and heats of fusion of the interstitial polymers, and the latter data being used to calculate fractional crystallinity. Both melting point and crystallinity are reduced as the weight fraction of guest polymer increases, crystallinity disappearing entirely in the case of the poly(methacrylic acid) interstitial. For this latter material, there is evidence for the formation of a complex between the poly(methacrylic acid) and the network chains.

Keywords Interstitial polymers; polyurethane; melting; crystallinity; network

INTRODUCTION

There is currently much interest in the preparation and properties of composite polymers containing two or more chemically distinct polymers[1-5]. The ultimate goal is to understand the factors of importance in determining the properties of such multicomponent polymers so that systems can be 'engineered' to produce the desirable properties. Apart from the investigation of the fundamental basis of polymer compatibility to produce single-phase multicomponent polymers[6], it is clear that phase-separated polymers (much the more common case) may be important materials for specific applications[7]. Consequently, the controlling factors which determine the structure of phase-separated blends are being investigated[8] and the morphological features of the well known styrene–isoprene block copolymers have been investigated in detail by small-angle X-ray[9] and small-angle neutron scattering[10-12].

Another method that has been used to produce multicomponent polymers is *via* the preparation of so-called interpenetrating networks[1-3,13]. In its broadest sense an interpenetrating network consists of two chemically distinct polymers, one of which is crosslinked, the other polymer which itself may be crosslinked being prepared in the presence of the network. In spite of the generic term 'interpenetrating network', many of the products have a two-phase structure and perhaps a more applicable description is that of interstitial polymers introduced earlier[14]. Though many such systems have been prepared and their properties studied[15,16], published descriptions have been confined to those systems where both components have always been amorphous. In general, semicrystalline polymers are tougher than amorphous polymers. Poly(ethylene oxide) is a typically semicrystalline polymer which is also water-soluble and may be crosslinked to a network via urethane crosslinks[17]. We report here the preparation of interstitial polymers using such a network with poly(methyl acrylate) and poly(methacrylic acid) as guest polymers in the host polyurethane network. In contrast to other interstitials, those reported here have crystallinity (in part) and we discuss this aspect of these materials.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG) was a hydroxyl end-grouped material with a nominal molecular weight of 6 kg mol^{-1} obtained frum Union Carbide. Determination of the hydroxyl number in our laboratory gave a number average molecular weight (M_n) of 8.5 kg mol^{-1}. This material was dried under reduced pressure at 383K for 4 h with a continuous stream of dry nitrogen passing through it. Additional materials for the preparation of the polyurethane network were 1,2,6-trihydroxyhexane, dried under vacuum at 383K, and 4,4-diphenylmethane diisocyanate (MDI) distilled at 453–463K under reduced pressure.

Methyl acrylate and methacrylic acid were dried and distilled under reduced pressure whilst 2,2-azobisiso-butyronitrile (AIBN) used as initiator was recrystallized from methanol.

Preparation of polyurethane network

For the preparation of the network a 1:1 molar ratio of hexane triol to PEG was used, the MDI quantity being the stoichiometric amount for complete reaction of the hydroxyl groups. The PEG and hexane triol were mixed together and heated at 363K for 30 min, the MDI being similarly heated in a separate container. All components

---

* Present address: Federal Institute of Industrial Research, Private Mail Bag 1023, Ikeja, Lagos State, Nigeria

† To whom correspondence should be addressed

0032—3861/83/030279–06$03.00

were then rapidly mixed with vigorous stirring and the resultant liquid poured into a preheated PTFE-lined mould. The mould was tightly covered and the network cured at 363K for 4 h, after which time it was cooled to room temperature. The polyurethane (PU) networks were opaque white blocks with dimensions of $10 \times 10 \times 2.5$ cm^3 and a total mass of ~250 g.

Preparation of interstitial polymers

The PU prepared as described above was cut into thin sheets with dimensions $5 \times 5 \times 0.15$ cm^3. After drying under vacuum at 313K for 24 h, the sheets were immersed in methyl acrylate or methacrylic acid containing 0.2% (w/w) AIBN for varying periods of time between 2 min and 8 h. After the allotted time the sheets were removed, surface dried by blotting, placed between two glass plates and tightly wrapped in polythene sheet. By this means sheets were obtained covering a wide range of swellings and hence monomer content. The monomer was allowed to disperse uniformly throughout the sheets over a period of 24 h, after which they were heated at 333K for 23 h and at 343K for 1 h. After cooling to room temperature, the sheets were removed from the glass plates and dried under vacuum at 313K to constant weight. The weight fraction of 'guest' polymer, i.e. poly(methyl acrylate) (PMA) or poly(methacrylic acid) (PMAA), was determined from the difference in weights of the final product and the initial network. The ranges of guest polymer weight fractions investigated were:

poly(methyl acrylate)	0–0.617
poly(methacrylic acid)	0–0.784

Determination of thermal properties

Crystalline melting points (T_m) and heats of fusion (ΔH_f) were obtained using a Du Pont 990 thermal analyser with a Du Pont 910 differential scanning calorimeter (d.s.c.) cell. Temperature calibration was made using pure indium, which melts at 429.6K. Similarly the calibration coefficient for calorimetry was also determined using indium since its heat of fusion is accurately known. For the determination of the polymer melting points, small samples were dried under vacuum at 313K for 24 h before being sealed into aluminium d.s.c. pans. The sample pan and an empty pan used as reference were then placed in the d.s.c. cell and cooled to 273K with liquid nitrogen. After 5 min equilibration at this temperature they were heated to 343K at a rate of 5K min^{-1}. Melting points were taken as the intersection of the extrapolated baseline and a tangent drawn to the leading edge of the melting endotherm. Heats of fusion were obtained from accurate melting endotherms using a heating rate of 10K min^{-1}. The temperature range was 293–343K, which permitted the accurate interpolation of the baseline in the region of the melting endotherms. The area of the melting endotherm was measured repeatedly using a planimeter and the results averaged. Heats of fusion, ΔH_f, were calculated using

$$\Delta H_f = \frac{AKC}{m} \quad \mathrm{J\,g^{-1}} \tag{1}$$

where A is the endotherm area (cm^2), K the calibration coefficient of d.s.c. cell (mW mV^{-1}), C the product of recorder time base and sensitivity of trace (mV min cm^{-2}) and m the weight of sample (mg).

Characterization of guest polymers

PU/PMA interstitials were Soxhlet extracted with chloroform for 72 h. The extract was then concentrated on a rotary evaporator and the extracted polymer precipitated by pouring the concentrated solution into petroleum ether. After redissolving in tetrahydrofuran and reprecipitating in water, the extracted polymers were dried under vacuum at 313K to constant weight.

The poly(methacrylic acid) was extracted from only one PU/PMAA interstitial which had a PMAA weight fraction of 0.784. This sample was Soxhlet extracted with methanol for 72 h. The extract was concentrated and added dropwise to a toluene solution of diazomethane, thus converting the poly(methacrylic acid), to poly(methyl methacrylate) (PMMA). However, methanol extraction did not remove all the PMAA from the interstitial, only some 34% of the original sample weight being removed by this extraction. The remaining PMAA was isolated by hydrolysing the residue after extraction by continuous stirring in 0.05 M sodium hydroxide solution for one week. The hydrolysate was then dialysed for one week to remove low molecular weight hydrolysis products, before the water was exchanged for the methanol on a rotary evaporator. The methanol solution was then added dropwise to diazomethane solution. Each of the solutions of PMMA so obtained was poured into separate portions of petroleum ether, redissolved in tetrahydrofuran and reprecipitated in water. After drying, the products were obtained as white powders.

Each of the extracts (PMA or PMMA) was examined by i.r. spectroscopy and number average molecular weights were determined by membrane osmometry. High-resolution (300 MHz) n.m.r. spectra were obtained for the PMMA extracts, this service being kindly performed by Dr F. Heatley of the University of Manchester.

RESULTS

Reproducibility of polyurethane network

Four individually prepared PU networks were prepared according to the methods described above. Samples from each were taken and the values for the melting point, heat of fusion and swelling in water at 298K determined, the values being given in *Table 1*. From the values in *Table 1*, properties associated with the crystallinity of the network chains (chiefly poly(ethylene oxide) (PEO)) show no significant variation from network to network. However, properties which are characteristic of the network, e.g. the equilibrium swelling, are not reproducible. This is not surprising since a major factor determining these properties is the crosslink density. Since no special precautions were undertaken to ensure identical conditions of network preparation, it is entirely

Table 1 Melting point (T_m), heat of fusion (ΔH_f) and swelling (S) for four PU networks

Network	T_m (K)	ΔH_f (kJ kg^{-1})	S (%)
1	322.0	92.69	384
2	320.0	99.13	517
3	322.5	102.32	563
4	320.5	99.15	632

conceivable that different networks will have different crosslink densities. It is thought that atmospheric moisture in conjunction with variations of mixing efficiency are the major source of this difference, since the MDI reacts with water to produce urea and biuret. MDI units which react in this way will not be able to participate in network formation, and hence some chain ends will not be incorporated into the network. Notwithstanding this variation from network to network, samples from within the same network had identical values of T_m, ΔH_f and swelling within experimental error. For these reasons in subsequent work on PMA/PU and PMAA/PU interstitial polymers, the samples for any one examination technique, e.g. determination of T_m were all prepared from the same host PU network.

Melting points

Typical melting endotherms for interstitials with PMA as guest polymer are shown in *Figure 1* and *Figure 2* shows the dependence of T_m on weight fraction of guest polymer. Both types of interstitial show a decrease in the PU melting point as the weight fraction of guest polymer increases, this decrease being particularly abrupt where PMAA is the guest polymer. Indeed, for this interstitial, no evidence of a crystalline melting point or endotherm could be detected above a PMAA weight fraction of ~0.4.

Heats of fusion

Heats of fusion calculated by the peak area method[18] were normalized to unit mass of crystallizable polymer (PU) and are quoted in *Table 2* together with the T_m values for each interstitial polymer. Fractional crystallinities have been calculated from these data from their ratio to the heat of fusion for fully crystalline polyethylene oxide, the major constituent of the PU network. For this purpose we have used a value of 220.12 kJ kg^{-1} as the heat

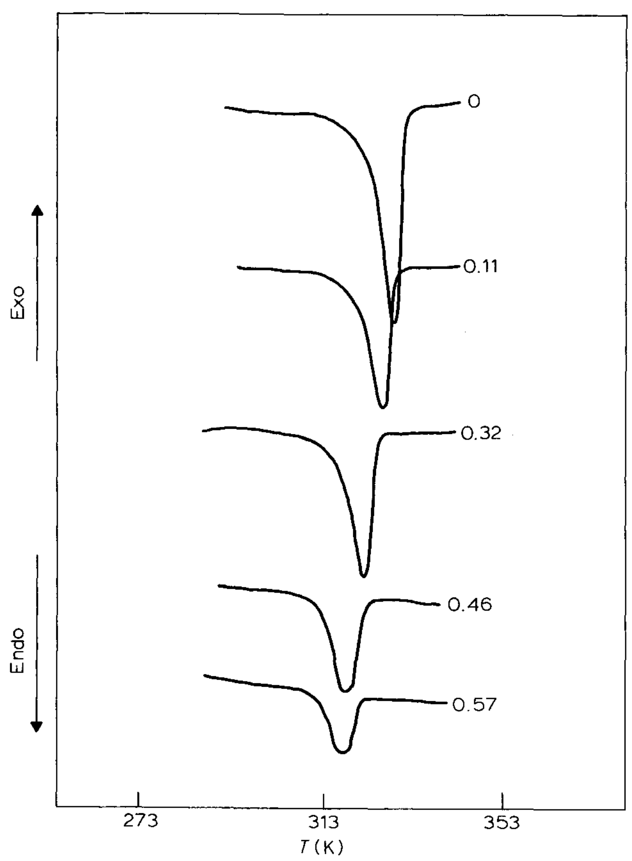

Figure 1 Melting endotherms for PMA/PU interstitial polymers; weight fraction of PMA is quoted on the curves, which are displaced vertically for clarity

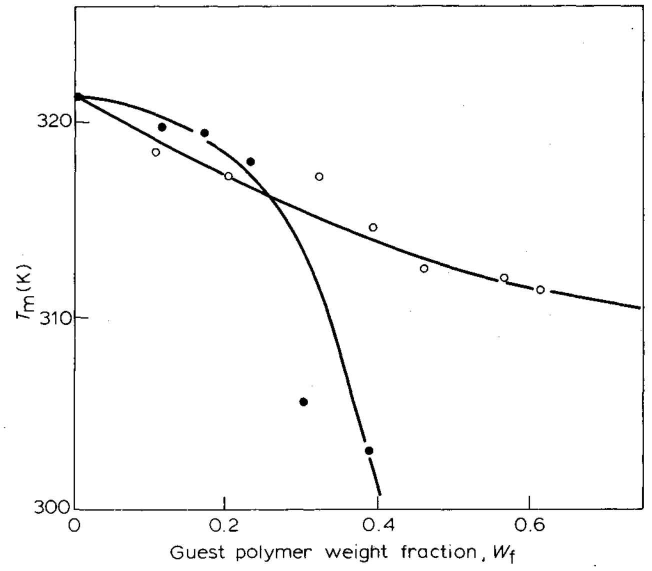

Figure 2 Variation of melting point with weight fraction of guest polymer: ○, PMA/PU; ●, PMAA/PU

Table 2 Thermal data for PMA/PU and PMAA/PU interstitial polymers

PMA/PU			PMAA/PU		
W_f PMA	T_m (K)	ΔH_f (kJ kg^{-1})	W_f PMAA	T_m (K)	ΔH_f (kJ kg^{-1})
0	321.34	98.32	0	321.34	98.32
0.11	318.45	78.64	0.117	319.95	55.4
0.204	316.65	80.95	0.173	319.65	45.8
0.324	316.65	61.49	0.233	318.15	32.14
0.399	314.65	62.11	0.305	305.75	13.83
0.462	312.55	56.21	0.39	303.15	–[a]
0.569	311.95	51.86	0.472[b]	–	–
0.617	311.45	52.7	0.572	–	–
			0.679	–	–
			0.784	–	–

[a] Endotherm area too small to measure accurately
[b] Neither T_m nor endotherms were observed for polymers with $W_f > 0.39$

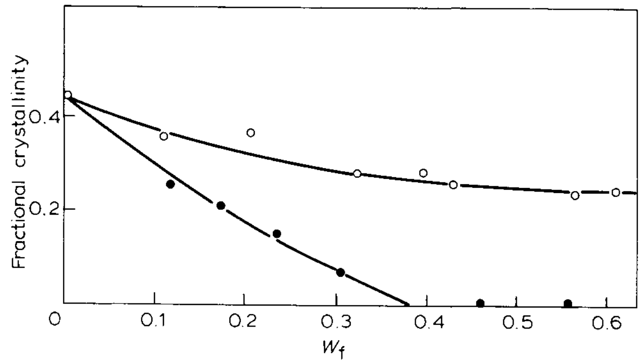

Figure 3 Variation of fractional crystallinity with weight fraction of guest polymer: ○, PMA/PU; ●, PMAA/PU

Table 3 Number average molecular weights (M_n) for PMA and PMMA extracts from interstitial polymers

(a) PMA/PU

W_f PMA	0.204	0.37	0.514	0.626
M_n (kg mol^{-1})	12.6	33.3	17.1	24.8

(b) PMAA/PU

	MeOH extract	Hydrolysate
W_f PMAA	0.784	0.784
M_n (kg mol^{-1})	100.3	119.7

of fusion for fully crystalline PEO calculated from the data of Braun *et al.*[19] *Figure 3* shows the dependence of fractional crystallinity on the composition of the interstitials.

Molecular characteristics of the guest polymer

Examination of the i.r. spectra of the extracted PMA showed the presence of polyurethane contamination, which may indicate some grafting of the guest polymers in the matrix. Additionally, complete removal of the guest PMA was not possible by simple Soxhlet extraction; contamination was generally slight, however. Number average molecular weights for the extracts are shown in *Table 3*, and *Figure 4* shows a typical gel permeation chromatogram of the PMA extracts. By contrast the PMMA extracts were unimodal when examined by g.p.c. The n.m.r. spectra of the PMMA obtained from the PMAA extracts were identical with similar spectra of PMMA prepared by conventional methods. Percentage tacticities were obtained from the integral heights of the isotactic, syndiotactic and heterotactic α-methyl group resonances at 8.83, 9.21 and 9.03 respectively. These values are slightly different from those quoted by Bovey and Tiers[20], the difference being attributable to our use of deuterated chloroform at room temperature as a solvent whilst the earlier values were obtained at 393K in chlorobenzene. *Table 4* shows the percentage tacticities determined in this way.

DISCUSSION

The depression of melting point for a semicrystalline polymer in the presence of a low molecular weight diluent was first analysed by Flory[21] and yields the well known equation

$$\frac{1}{T_\mathrm{m}}-\frac{1}{T_\mathrm{m}^\circ}=\frac{RV_2}{\Delta H_2 V_1}(\varphi_1-\chi\varphi_1^2) \qquad (2)$$

where T_m° is the melting point in the absence of diluent, V_i the molar volume of the repeat units in the diluent ($i=1$) and the crystallizing polymer ($i=2$), ΔH_2 the molar heat of fusion for perfectly crystalline repeat units, χ the crystallizing polymer–diluent interaction parameter and φ_1 the volume fraction of diluent.

Equation (2) has been modified by Nishi and Wang[22] for the case of macromolecular diluent which is miscible with the semicrystalline polymer in the liquid state but immiscible in the crystalline state. In these cases equation (2) becomes

$$\frac{1}{T_\mathrm{m}}-\frac{1}{T_\mathrm{m}^\circ}=\frac{RV_2}{\Delta H_2 V_1}\chi\varphi_1^2 \qquad (3)$$

Equation (3) therefore predicts that a melting point depression will only occur when the two polymers are compatible in the liquid state. Furthermore, a plot according to equation (3) should be a straight line passing through the origin. This type of plot for the present data is shown in *Figure 5*; neither set of data is in good agreement with the description of equation (3).

Recourse may be made to equation (2) on the premise that, since the molecular weight of the PU network is essentially infinite whilst that of the guest polymers (especially PMA) is finite, then they may be acting in the same role as low molecular weight diluents. *Figure 6* shows the melting point data plotted in this manner and the data for PMA follow the expected behaviour, i.e. a straight line of negative slope. The molar heat of fusion calculated from the intercept is 12.7 kJ mol^{-1}, in good agreement with quoted values[21,23] for PEO which range

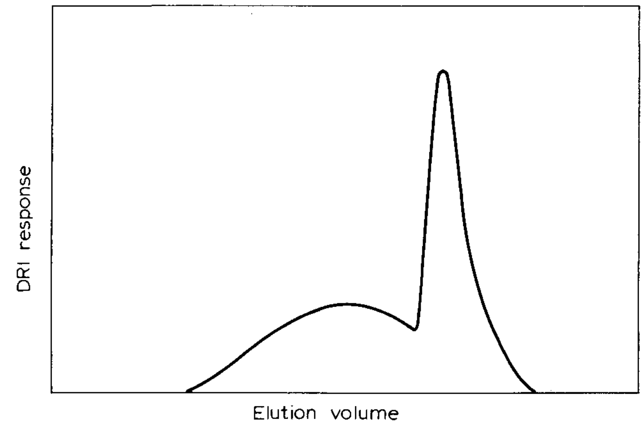

Figure 4 Typical gel permeation chromatogram for PMA extract from an interstitial with a PMA weight fraction of 0.37

Table 4 Percentage tacticities obtained for PMA extracts from PMMA/PU interstitial

Source of PMMA	Iso-tactic	Syndio-tactic	Hetero-tactic
Methanol extract	10.6	48.8	40.6
Hydrolysate	17.5	46.8	35.7

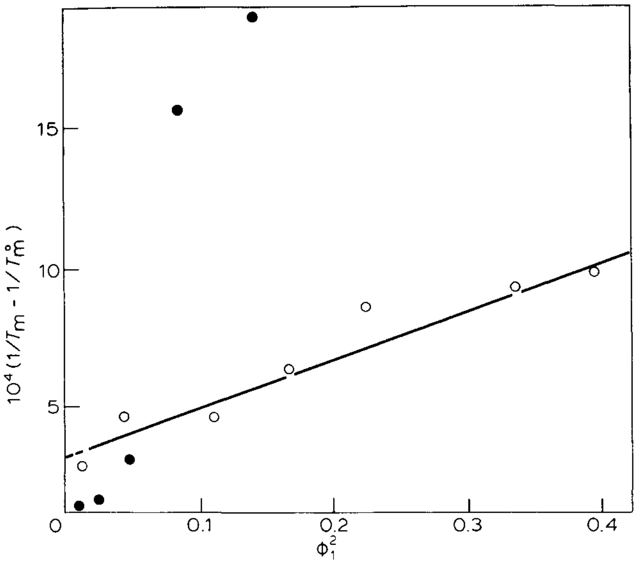

Figure 5 Melting point data plotted according to the equation of Nishi and Wang (equation (3)): ○, PMA/PU; ●, PMAA/PU

from 8 to 16 kJ mol^{-1}, whilst the slope gives 0.3 as the value of the interaction parameter χ. The magnitude of this value indicates gross incompatibility between the PMA and PU, since compatibility usually requires negative values of χ to accommodate the vanishingly small entropic contribution to polymer miscibility[24-26].

The reasonable values for the molar heat of fusion and the interaction parameter are encouraging. However, this approach is much too simplistic to be the basis of an analysis of the PMA/PU interstitial. What has to be considered are the total free energy changes involved in interstitial formation compared to the total free energy of the two separate components. At this stage we can only present a qualitative description which may be applicable, but it does point out areas where further experimental effort is required. Initially at some high temperature we assume the interstitial is totally amorphous and randomly mixed and the free energy change involved includes a mixing term (ΔG_m) and an elastic free energy (ΔG_{el}) due to network swelling by the guest polymer. In the final state at a lower temperature there is crystalline host polymer, guest polymer in domains of some form and amorphous host polymer. The free energy changes involved here are that for crystallization (ΔG_c), phase separation of guest polymer (ΔG_{ps}) and domain formation of the guest polymer. The net free energy change is the sum of all these terms.

The elastic free energy may be expressible using the Flory–Rehner equation, whilst the sum of the mixing and phase-separation terms will result in a term involving the number of guest polymer domains and molecules present. Such a simple formulation for the free energy of domain formation will not occur since this will include a surface free energy term due to the interaction between domain and matrix, which will be dependent on domain size, plus an incompressibility term descriptive of the need to maintain uniform density in the guest polymer domains.

The free energy change on crystallization is expressible in terms involving the observed melting point, the melting point of large (in the limit, infinitely large) crystals, the fold surface free energy and the crystal lamellar thickness.

If equilibrium conditions obtain, and this may be questionable in interstitials, then this sum of terms has to be minimized with respect to domain size, lamellar thickness, fold surface free energy and melting point. At this stage such a minimization is not feasible and consequently we cannot progress further with the description of the PMA/PU interstitials.

For PMAA/PU interstitials we are able to be a little more specific, since there is evidence for the formation of a complex between the PMAA and the PEO, a phenomenon which has been reported for aqueous solutions of PMAA and PEO. There is some ambiguity regarding the composition of this complex. Bailey *et al.*[27] indicate a 3:1 molar ratio of ethylene oxide to methacrylic acid units, whilst both Antipina *et al.*[28] and Ohno *et al.*[29] conclude that the complex has a 1:1 molar ratio. If such a complex is formed, then the depression in melting point can be rationalized using the analysis of Brown and Eby[30] for polyethylene and subsequently used by Bassett and Carder[31]. The melting point in a pure semicrystalline polymer is related to the maximum melting temperature, T_m°, the heat of fusion per unit volume, ΔH_2, the fold surface free energy, σ_e, and the crystalline lamellae thickness, l:

$$T_m = T_m^\circ\left(1 - \frac{2\sigma_e}{l\Delta H_2}\right) \qquad (4)$$

This equation is based on the crystallization occurring in folded chain lamellae. Since PEO does crystallize in this manner, the lamellar thickness being approximately 100 Å,[32] we can apply it to the present results. Assuming that a complex is formed between the PMAA and PEO which does not crystallize, then the presence of this complex in the amorphous phase surrounding the lamellae will clearly influence the value of σ_e, the fold surface free energy; in particular it has to increase σ_e so that T_m is reduced.

The fold surface free energy in a semicrystalline polymer is equivalent to the interfacial energy between two chemically distinct polymers. In the absence of specific interactions across the phase boundary, interfacial energy generally increases as the difference in polarity between the two polymers increases[33,34]. Clearly, the formation of a PEO/PMAA complex will increase the polarity of the amorphous phase and an increase in the fold surface free energy with a consequent reduction in T_m is indeed possible. Although this explanation may be valid, it is clear from *Figure 3* that the crystallinity of the PMAA/PU interstitials is rapidly reduced by the presence of the PMAA, even after normalization to unit weight of

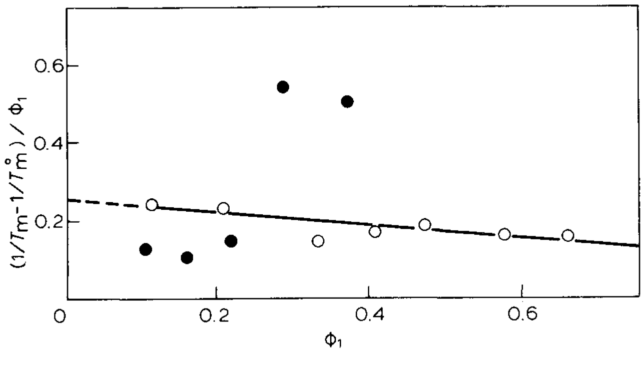

Figure 6 Melting point data plotted according to the equation of Flory (equation (2)): ○, PMA/PU; ●, PMAA/PU

PU. During polymerization of the PMAA, it appears that the PEO/PMAA complex formed prevents the PEO crystallization, hence reducing the fractional crystallinity. The extrapolated value of the weight fraction of PMAA at which crystallinity apparently disappears is 0.39, which corresponds to a molar ratio of ethylene oxide units to methacrylic acid units of 3:1, in excellent agreement with the value deduced by Bailey *et al.*[27] However, it was noted in the extraction of PMAA from the interstitial that some PMAA could not be removed by this means. At this point the composition of the extracted PMAA/PU interstitial was such that the molar ratio of ethylene oxide units to methacrylic acid units was 1:1, a figure obtained by other workers using aqueous mixtures of PMAA and PEO[28]. The tacticities of the two poly(methyl methacrylate)s obtained from the PMAA extracts are sufficiently different to be worthy of comment. In particular, the greater proportion of isotacticity in the hydrolysate product indicates that some of the methacrylic acid monomers have adopted a specific conformation prior to polymerization. It has been postulated that the bonding site for complex formation between PEO and PMMA is a hydrogen bond between the ether oxygen and the proton in the carboxylic acid group[28]. Clearly such interactions could also prevail for the case of monomeric methacrylic acid and PEO. In the crystalline state PEO molecules have a deformed helical structure with seven monomer units for every two turns of the helix which has an identity length of 19.48 Å, the ether oxygen atoms being directed to the fibre axis[35]. Since polymerization of the methacrylic acid was carried out at a temperature only some 10K above the melting point of the PU network, then it is possible that the helical structure of the PEO molecule may not have been completely destroyed* and may therefore act as a 'template' for the stereospecific polymerization of the methacrylic acid. Such molecules cannot be present in a large quantity since the difference in tacticities between the two extracts is not large.

The reduction in fractional crystallinity for the PMA/PU interstitials is not so great as for the PMAA/PU material and the crystallinity approaches an asymptotic limit.

There appears to be no evidence for the formation of a complex between PMA and PEO, but the presence of PU in the extracted PMA suggests that some of the PMA is grafted to the PU network chains. Such grafted chains may then be prevented from crystallizing. Acrylic monomers are particularly prone to chain transfer reactions[37] and methyl acrylate polymerization results in branched polymer being formed unless conversions are kept very low[21]. Grafting may thus be brought about by chain transfer to PU chains creating sites from which grafted chains may grow. Such transfer reactions may be the reason for the low values of molecular weight recorded in spite of the polymerization taking place in a viscous medium which usually promotes production of high molecular weight polymer.

ACKNOWLEDGEMENTS

I. Aladesulu thanks the Government of the Federal Republic of Nigeria for a Scholarship. Thanks are also due to Dr F. Heatley, Department of Chemistry, University of Manchester, for the n.m.r. spectra.

REFERENCES

1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum Press, New York, 1976

2 Klempner, D. and Frisch, K. C. 'Polymer Alloys', Plenum Press, New York, 1977

3 Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New York, 1978

4 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

5 Eirich, F. R. *Pure Appl. Chem.* 1976, **46**, 115

6 Allen, G. NATO Advanced Study Institute, University of Strathclyde, 1981, to be published

7 Aggarwal, S. L. *Polymer* 1976, **17**, 938

8 Carter, A. and Higgins, J. S. 'Small Angle Scattering from Heterophase Systems', Biennial Polymer Physics Meeting, Reading, England, 1981

9 Hashimoto, T., Shibayoma, M. and Kawai, H. *Macromolecules* 1980, **13**, 1237

10 Richards, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581

11 Richards, R. W. and Thomason, J. L. 'Small Angle Scattering from Heterophase Systems', Biennial Polymer Physics Meeting, Reading, England, 1981

12 Thomason, J. L. *Ph.D. Thesis*, University of Strathclyde, 1981

13 Sperling, L. H. *J. Polym. Sci. Macromol. Rev.* 1977, **12**, 141

14 Allen, G., Bowden, M. J., Blundell, D. J. and Hutchinson, F. C. *Polymer* 1973, **14**, 597

15 Hourston, D. J. and McCluskey, J. A. *Polymer* 1979, **20**, 1573

16 Yeo, J. K., Sperling, L. H. and Thomas, D. A. *J. Appl. Polym. Sci.* 1981, **26**, 3283 (and cognate references)

17 Graham, N. B., Nwachuku, N. E. and Walsh, D. J. *Polymer* 1982, **23**, 1345

18 Blundell, D. J., Beckett, D. R. and Willcocks, P. H. *Polymer* 1981, **22**, 704

19 Braun, W., Hellwege, K. H. and Knappe, W. *Kolloid Z.* 1967, **215**, 10

20 Bovey, F. A. and Tiers, G. V. D. *J. Polym. Sci.* 1960, **44**, 173

21 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

22 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

23 Miller, R. L. in 'Polymer Handbook', 2nd Edn. (Eds. J. Brandrup and E. H. Immergut), Wiley Interscience, New York, 1975

24 Krause, S. *J. Macromol. Sci. C* 1972, **7**, 251

25 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279

26 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690

27 Bailey, F. E., Lundberg, R. D. and Callard, R. W. *J. Polym. Sci. A* 1964, **2**, 845

28 Antipina, A. B., Baranovsky, Y. Y., Papisov, I. M. and Kabanov, V. A. *Polym. Sci. USSR* 1972, **14**, 1047

29 Ohno, H., Matsuda, H. and Isuchida, E. *Makromol. Chem.* 1981, **182**, 2267

30 Brown, R. G. and Eby, R. K. *J. Appl. Phys.* 1964, **35**, 1156

31 Bassett, D. C. and Carder, D. R. *Phil. Mag.* 1973, **28**, 513

32 Wunderlich, B. 'Macromolecular Physics', Vol. 1, Academic Press, New York, 1973

33 Cherry, B. W. 'Polymer Surfaces', Cambridge University Press, Cambridge, 1981

34 Wu, S. *J. Macromol. Sci. C* 1974, **10**, 1

35 Tadokoro, H. 'Structure of Crystalline Polymers', Wiley-Interscience, New York, 1979

36 Maxfield, J. and Shepherd, I. W. *Polymer* 1975, **16**, 505

37 Huglin, M. B. and Richards, R. W. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 1363

---

* In a Raman scattering study of poly(ethylene oxide), Maxfield and Shepherd[36] conclude that although the helical structure of the crystalline chain is lost on melting, some ordering is retained since complete conversion to a random coil configuration is not observed.