Polyhydroxyether–polydimethylsiloxane graft copolymers: 2. Properties and morphology

Aidan T. Holohan*, Maurice H. George† and James A. Barrie
Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

and David G. Parker
ICI Advanced Materials, Wilton, Cleveland TS6 8JE, UK
(Received 21 May 1993)

A series of polyhydroxyether-polydimethylsiloxane (PDMS) graft copolymers were analysed and tested to determine the effects of factors such as the number-average molecular weight ($\bar{M}_n$) of the PDMS segments, overall PDMS content and nature of the graft linkage on thermal characteristics, hydrolytic stability, tensile properties and morphology. D.s.c. measurements showed that the copolymers exhibit two-phase morphology even at very low PDMS $\bar{M}_n$ ($<1000\,\mathrm{g\,mol^{-1}}$). Despite the presence of the silyl ether linkage, such copolymers display quite good hydrolytic stability. When the PDMS $\bar{M}_n$ is in the region of $5000\,\mathrm{g\,mol^{-1}}$, changes in the overall composition have only a marginal effect on thermal stability.

(Keywords: graft copolymer; polydimethylsiloxane; polyhydroxyether)

INTRODUCTION

Previously, we reported the synthesis of well defined polyhydroxyether–polydimethylsiloxane (PDMS) graft copolymers[1]. These copolymerizations were based on the coupling of appropriate functional groups on preformed polymers. A number of synthetic pathways were investigated, including hydrosilation and the alcoholysis of silyl chlorides, to determine their relative effectiveness and the implications of the resulting graft linkage on the physical properties of the bulk material. This paper describes the effects of factors such as the number-average molecular weight ($\bar{M}_n$) of the PDMS segments, overall PDMS content and nature of the graft linkage on thermal characteristics, hydrolytic stability, tensile properties and morphology.

Although there have been numerous studies of polysiloxane block and graft copolymers, detailed investigations of the morphology and structure–property relationships of these systems have received only limited attention. The bulk of these investigations have focused on PDMS. The non-polar nature of the PDMS structure together with the very low levels of intermolecular attractions lead to the formation of thermodynamically and mechanically incompatible blends with virtually all other polymeric systems. This is reflected in the very low solubility parameter of PDMS ($\delta = 14.9\,\mathrm{J^{1/2}\,cm^{-3/2}}$) when compared to other polymers ($\delta = 17.6$–$28.6\,\mathrm{J^{1/2}\,cm^{-3/2}}$) and is the main driving force in the formation of two-phase morphologies in PDMS copolymers. Thus the influence of segment lengths and segment crystallinity in obtaining two-phase morphologies is not as critical as in other copolymer systems. By altering the chain length or mole fraction of PDMS a variety of copolymers with properties varying from thermoplastic elastomers to rubber modified thermoplastics can be obtained.

In addition to the mole fraction of PDMS, the type of morphology is also dependent on the method of specimen fabrication. TEM investigations have shown that the microphase morphology of certain solvent cast PDMS copolymer films are considerably affected by the choice of solvent[2–4]. This particular technique is a very effective means of controlling morphology and related properties.

EXPERIMENTAL

Measurements

D.s.c. measurements were performed on a Du Pont 910 differential scanning calorimeter using a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. Thermogravimetric analysis (t.g.a.) was carried out using a Stanton Redcroft TG 750 thermobalance using a heating rate of $30^\circ\mathrm{C\,min^{-1}}$ and N_2 flow rate of $10\,\mathrm{cm^3\,min^{-1}}$. Isothermal measurements were also performed under N_2 using a similar heating ramp. At the set temperature, samples were held for between 0.5 h and 1.5 h. Electron microscopy examination of the copolymers was carried out at ICI Wilton (UK) on a Philips CM12 transmission electron microscope using an accelerating voltage of 100 keV. Ultrathin sections of solvent-cast (tetrahydrofuran, THF) samples were obtained using a Reichert Ultracut E device. Owing to the difficult nature of the copolymers, samples were either embedded in epoxy resin prior to sectioning or sectioned using a

---

* Present address: Paint Research Association, Teddington, Middlesex, UK

† To whom correspondence should be addressed

0032-3861/94/05/0977-06

cryostage where appropriate. Tensile testing of the copolymers was also carried out at ICI Wilton, using an Instron 6022 series mechanical tester. Tests were conducted using a crosshead speed of 5 mm min^{-1}, gauge length of 25 mm and average sample cross-sectional area of 0.5×4.0 mm^2. Both solvent-cast and compression-moulded samples were examined.

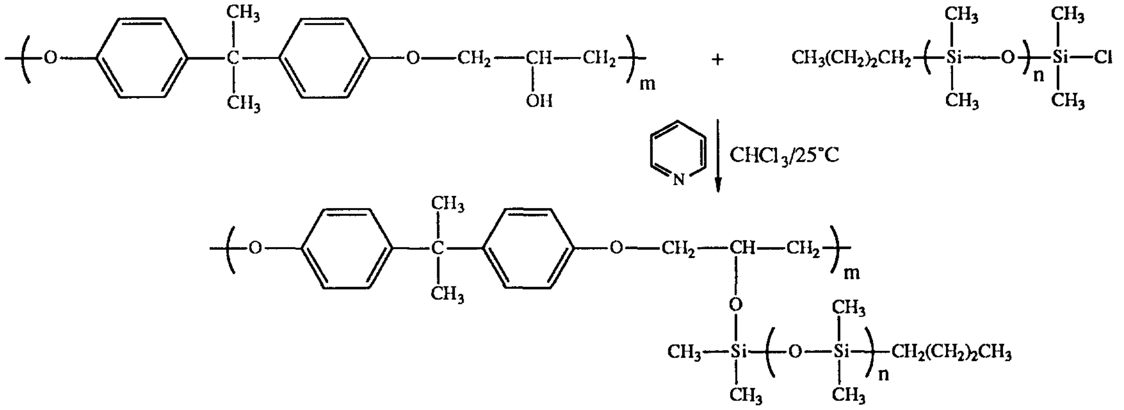
RESULTS AND DISCUSSION

The polyhydroxyether described herein refers to the reaction product of bisphenol A and epichlorohydrin. This is more commonly referred to as phenoxy. Unless otherwise stated, the phenoxy used in this work was a commercial material donated by Union Carbide Corp. and is designated PKHJ. It has a determined $\bar{M}_n$ of 27 300 g mol^{-1} and a polydispersity of 2.93[4]. PKHJ-AL refers to allyl derivatized PKHJ. The synthesis of the graft copolymers are shown in *Schemes 1* and *2*.

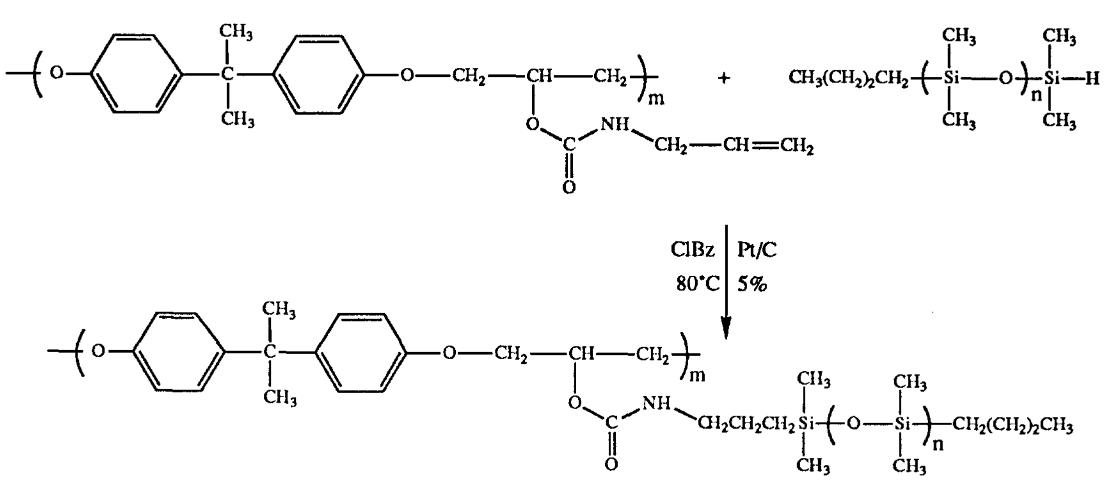
Thermal characteristics

Thermal analysis of the graft copolymers was carried out using d.s.c. dynamic mechanical thermal analysis and t.g.a. As expected of copolymer systems comprising PKHJ and PDMS, where there is a high degree of incompatibility, phase separation occurs at very low PDMS graft lengths ($\bar{M}_n < 1000$ g mol^{-1}). This was indicated from the d.s.c. thermograms where two distinct glass transitions were observed for each graft copolymer. The thermograms are strongly affected by the mole fraction of PDMS. At high siloxane compositions (>70%), in addition to the respective glass transition temperatures (T_gs) of the two components, both the cold crystallization and crystalline melting peaks of PDMS are also observed. Apparently at low PKHJ levels, crystallinity is not significantly disrupted. Increasing the weight fraction of PDMS gives rise to a considerable depression of the PKHJ T_g. This effect is more pronounced in copolymers containing shorter PDMS segments. This trend is also apparent in the spread of glass transition (ΔT_g) for each component. The relative increase in the PDMS T_g (5–25°C) would appear to result from the restriction of molecular motion of the linear polymer chains accompanying graft copolymerization. Increasing the mole fraction of PKHJ does not significantly affect the T_g of PDMS, although a slight increase is apparent. The results are summarized in *Table 1*. Transitions for the parent homopolymers are also included for comparison.

These observations are in good agreement with the findings of Cameron and Chisholm[5] who studied a similar system using polystyrene as the backbone. They attributed the more pronounced effects of the short chain grafts at higher densities to the interpenetration of the two components resulting in more diffuse phase boundaries (wider ΔT_g). Tyagi *et al.*[6] have reported similar observations for the polysulfone (PSU)–PDMS block copolymer system. In many cases the value of ΔT_g was found to be as high as 60°C. Once again this was



Scheme 1 Series 4 graft copolymers containing a silyl ether linkage



Scheme 2 Series 3 graft copolymers prepared via hydrosilation

Table 1 Thermal characteristics of a series of PKHJ–PDMS graft copolymers and their homopolymer precursors

			PDMS (°C)				PKHJ (°C)	
Sample	PDMS, M_n[a]	% PDMS[a]	T_g	ΔT_g	T_c	T_m	T_g	ΔT_g
PPMS-H	1320	–	−129	5	−92	−34[b]	–	–
4J	838	27.0	−109	24	–	–	72	31
4G	965	38.5	−112	20	–	–	57	26
3B	1320	68.5	−116	25	−94[d]	−35	36	23
PDMS-H	3100	–	−125	3	−90	−30[b]	–	–
PKHJ	–	–	–	–	–	–	88	7
4L	3150	11.5	−105	12	–	–	83	9
4K	2560	42.0	−115	8.0	–	–	68.5	16
4I	2800	55.7	−117	5.0	–	–	65	10
4M	2738	59.0	−117	6.5	–	−33[c]	55	14
4F	2872	84.7	−118	3.0	−84	−34	–	–[d]

[a] Determined using ^{1}H n.m.r. spectroscopy

[b] Bimodal, value given is that of most intense peak.

[c] Very weak feature

[d] No distinct T_g

attributed to large-scale phase mixing and development of an interfacial region between the hard and soft segments. Presumably similar effects are responsible for the glass transition behaviour in the PKHJ–PDMS copolymers. Some copolymer samples were also analysed using d.m.t.a. The results were generally consistent with the d.s.c. measurements. In addition, the d.m.t.a. thermograms revealed a progressive reduction of the PKHJ secondary loss peak (−56°C) as the grafting frequency increased. This was apparently due to the loss of mobility of the aliphatic ether linkage as a result of the presence of the substituent PDMS side chains.

The thermal stability of the copolymers was examined in a N$_2$ atmosphere under both dynamic and isothermal conditions. All copolymer samples displayed a single-stage decomposition profile. Surprisingly, although the Si–O–C linked copolymers display improved thermal stability relative to their PKHJ(AL)–PDMS analogues as a result of the inherent instability of the carbamate linkage, this improvement was considerably less than would be expected. For example, the onset of decomposition of PKHJ(AL)–PDMS 3B at 275°C was only 10°C lower than that for PKHJ–PDMS 4G. The $\bar{M}_n$ of PDMS in both cases is $\approx 1000\,\mathrm{g\,mol^{-1}}$. The presence of the siloxane chains obviously inhibits the breakdown of the carbamate linkage as evidenced by the single-stage decomposition profile; allyl derivatized phenoxy resin exhibits a two-stage decomposition profile, the initial weight loss at 190°C resulting in the regeneration of allyl isocyanate and the parent phenoxy resin. The molecular weight of the PDMS chains also has a profound effect on the onset of decomposition. In general, an increase in $\bar{M}_n$ gives rise to an increase in the onset of decomposition. The thermal stability of PDMS only becomes comparable with PKHJ at $\bar{M}_n$ values approaching $5000\,\mathrm{g\,mol^{-1}}$. When the $\bar{M}_n$ of PDMS is in this region, changes in composition have a marginal effect on the thermal stability of the copolymer. The effect of graft linkage and the $\bar{M}_n$ of the PDMS segments on thermal stability are depicted in *Figure 1*.

Isothermal measurements were performed by heating samples to set temperatures and monitoring the sample weight as a function of time. Once again the Si–O–C linked copolymers displayed only slightly improved thermal stability. At 270°C, both 3B and 4G were relatively quickly decomposed showing a 15% weight loss after 30 min. 4M however, showed only a 2% weight loss after 30 min at 300°C. These results are summarized in *Table 2*.

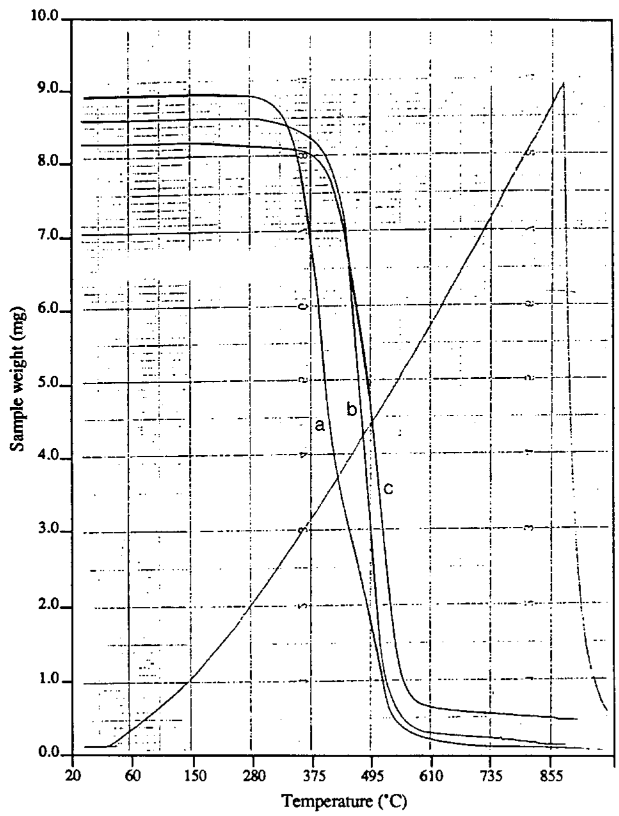


Figure 1 Effect of PDMS $\bar{M}_n$ and the nature of the graft linkage on the thermal stability of PKHJ–PDMS graft copolymers in N$_2$: (a) 4G; (b) 3B; (c) 4M

Table 2 Effect of graft linkage and PDMS $\bar{M}_n$ on the thermal stability of PKHJ–PDMS graft copolymers

Sample	Temperature (°C)	% weight loss after 15 min	% weight loss after 30 min
3B	270	7.5	15
4G	270	6	13
4M	300	–	2

Hydrolytic stability

Hydrolytic stability of the graft linkage may be an important consideration, depending on the particular application of the copolymer. Although it is widely recognized that the Si–O–C grouping is hydrolytically unstable, the susceptibility to hydrolysis varies greatly depending on the structure. For the vast majority of cases cleavage occurs at the Si–O bond and in general an increase in the electronegativity of the substituents attached to either the silicon or oxygen atoms increases the rate of hydrolysis. In siloxane-containing copolymers, the situation is more complex and other factors such as steric hindrance, the relatively low concentration of Si–O–C bonds and the hydrophobic nature of the siloxane segments must be considered. The upper T_g of the copolymer may also be critical if it is below the boiling point of water.

For the purposes of this investigation, compression-moulded thin films of the PKHJ–PDMS graft copolymers were immersed in boiling water for periods of up to 2 weeks. Samples were withdrawn periodically and after washing with methanol, followed by extraction with n-hexane and drying under vacuum (50°C), they were subjected to i.r. analysis. After determining the relative proportion of PDMS in each sample, a plot of PDMS mole fraction *versus* time was constructed (*Figure 2*).

Of the samples analysed, a 10–12% reduction in PDMS content was observed after immersion in boiling water for 2 weeks. No significant weight loss was observed in those copolymers prepared by hydrosilation. Due to the relatively low T_g of copolymers containing high PDMS content, only samples of low to medium PDMS content were examined. On this evidence, the copolymers display moderate resistance to hydrolysis. Although information on other Si–O–C linked PDMS graft copolymers is limited, a number of PDMS block copolymers have been investigated. The results are in good agreement with the findings of both Noshay *et al.*[7] and Wheatley[8] who carried out similar investigations on PSU–PDMS and poly(ether ether ketone) (PEEK)–PDMS block copolymers, respectively. Once again, resistance to hydrolysis was attributed to the low concentration of Si–O–C bonds and the shielding effect of the adjacent hydrophobic PDMS segments. It is likely that these factors also contribute to the hydrolytic stability of PKHJ–PDMS graft copolymers. On the other hand, the relatively low T_g of the samples examined (55–70°C) would be expected to increase the rate of diffusion and thus facilitate hydrolysis. Morris[9] has reported that poly(ether sulfone) (PES)–PDMS block copolymers display very poor hydrolytic stability, breaking down to simple homopolymeric mixtures in strong hydrogen bonding solvents. Although this has been attributed to the increased polarization of the Si–O bond by the electron withdrawing sulfone group, it is more likely that the overriding factor was the homogeneous conditions employed. Strong hydrogen bonding solvents such as dimethylsulfoxide or dimethylformamide normally pick up enough water to cleave Si–O–C bonds, even at room temperature.

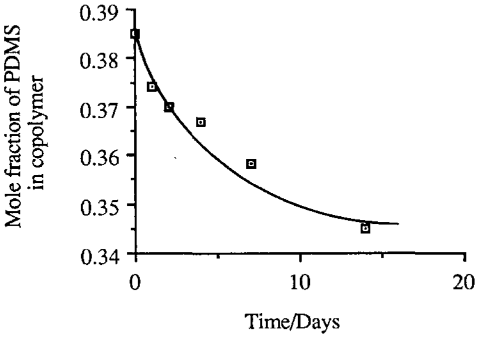


Figure 2 Hydrolytic stability of PKHJ–PDMS graft copolymer, 4G

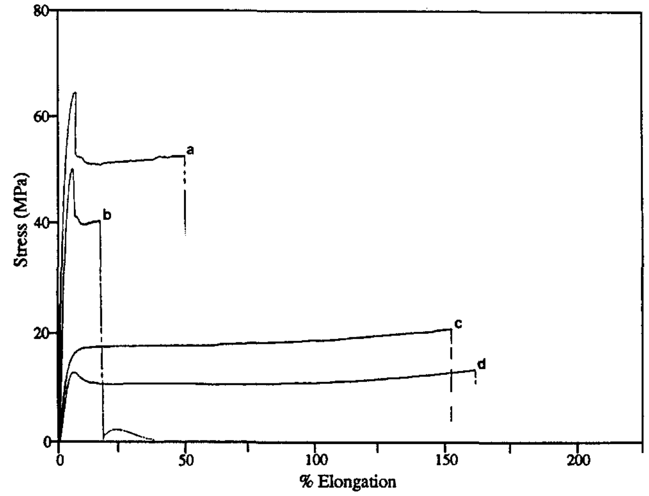


Figure 3 Stress–strain behaviour of a series of compression-moulded PKHJ–PDMS graft copolymers as a function of PDMS content and their comparison with the parent PKHJ: (a) PKHJ; (b) 4L; (c) 4J; (d) 4G

Tensile properties

Tensile test specimens of the graft copolymers were prepared by both solvent casting and compression moulding. Solvent cast films were obtained by the slow evaporation of a solution (20% w/v) of the graft copolymers in THF (a mutual solvent for both segments) under vacuum at room temperature. The resulting films were then dried under vacuum at ≈40°C for periods of up to 1 month. All films, with the exception of 4J and 4H, displayed a high degree of transparency. Both 4J and 4H were slightly hazy. 4H displayed uncharacteristically high recovery properties probably resulting from some degree of crosslinking in the material.

Attempts to prepare well formed compression-moulded films of the graft copolymers with siloxane contents in excess of 40%, proved difficult due to the poor cohesive nature of the materials. Although some improvement was apparent at higher temperatures (>260°C), some degradation was also noticeable. It should be mentioned that this upper limit was only possible with copolymers containing short graft chains ($\approx 1000\,\mathrm{g\,mol^{-1}}$) and that similar problems were observed at this composition level where the $\bar{M}_n$ of the PDMS segments was $\approx 3000\,\mathrm{g\,mol^{-1}}$.

As expected the tensile properties are affected not only by the mole fraction of the two components but also by the $\bar{M}_n$ of the PDMS segments. Increasing the $\bar{M}_n$ of PDMS gives rise to a depression of the yield stress and a corresponding increase in the percentage elongation for a constant PDMS mole fraction. *Figures 3* and *4* show the stress–strain curves for the compression-moulded and solvent-cast samples, respectively. For comparison, the corresponding PKHJ curves are also included.

Immediately evident is the unusual behaviour of 4L.

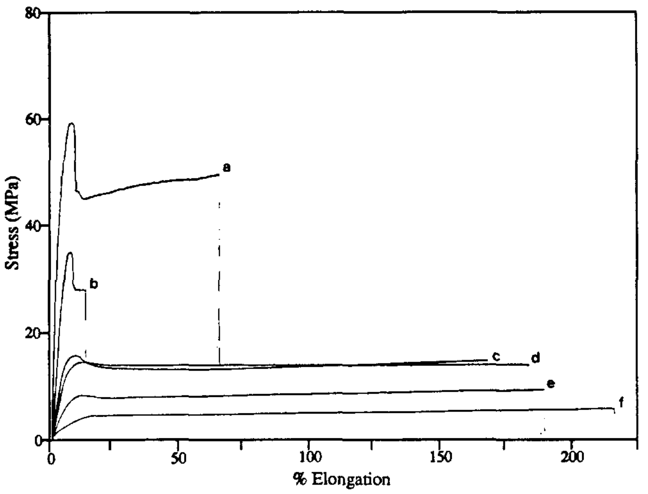


Figure 4 Stress–strain behaviour of a series of solvent cast PKHJ–PDMS graft copolymers as a function of PDMS content and their comparison with the parent PKHJ: (a) PKHJ; (b) 4L; (c) 4G; (d) 4K; (e) 4I; (f) 4M

Although graft copolymerization does result in a significant decrease in tensile strength, in contrast to the other samples the tensile elongation is also considerably reduced. Similar observations have also been reported by Nagase *et al.*[10] for the PSU–PDMS graft copolymer system, where the PDMS content was 18%. It would appear that in such compositions the concentration of PDMS is insufficient to create significant heterophase domains. As a result, instead of forming a network structure, the graft chains serve only to disrupt the intermolecular interactions of the backbone polymer.

Morphology

It is widely recognized that the unique properties of block and graft copolymers are directly related to their morphology[11–14]. Thus a knowledge of copolymer morphology is integral to understanding structure–property relationships. Various techniques have been used for studying the detailed morphology of heterophase copolymers including X-ray scattering, neutron scattering and TEM. Fortunately, there is an excellent contrast between the phenoxy and PDMS phases, which makes this copolymer system ideal for TEM studies.

Ultrathin sections of low siloxane content copolymers were prepared by embedding in epoxy resin and subsequent room temperature ultramicrotomy. Representative electron micrographs of 4L ($\approx 10\%$ PDMS) are presented in *Figures 5* and *6*. At magnifications of up to 70 000, the TEM image did not reveal any structural information which could be interpreted as microdomains. It is likely that the mole fraction of PDMS is insufficient to form significant heterophase microdomains. This would explain the poor mechanical properties displayed by this copolymer described in the preceding section. At very high magnifications, some fine structure is apparent and a speckled type of morphology can be observed. The sizes of the darker domains were estimated to be in the region of 5–12 Å. Assuming these are the PDMS domains (higher electron density[15]), the sizes are in good agreement with the radius of gyration ($R_g = 6.1$ Å) calculated on the basis of the number of repeat units in the PDMS chain, i.e. ≈ 40. There also appears to be a degree of order to the PDMS domains with banded/ribboned regions clearly evident.

Due to the relatively low T_g and poor cohesive nature of the copolymers of intermediate composition, sectioning was carried out using cryoultramicrotomy. The sections produced were ≈ 700 Å in thickness. Despite these

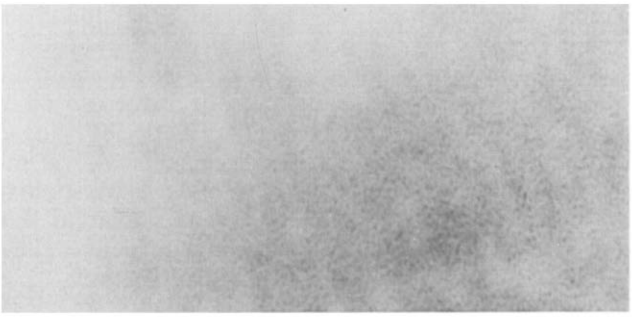


Figure 5 Transmission electron micrograph of PKHJ–PDMS graft copolymer, 4L (PDMS content $\approx 10\%$, PDMS $\bar{M}_n \approx 3000\,\mathrm{g\,mol^{-1}}$). Magnification: ×72 000

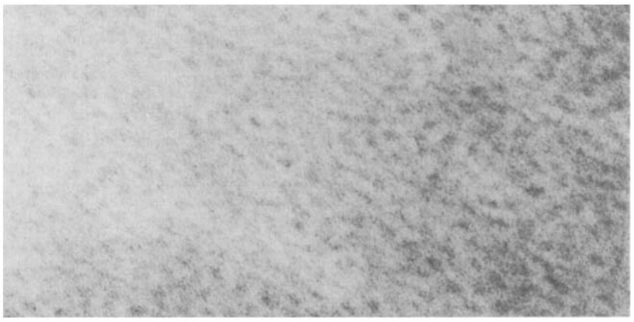


Figure 6 Transmission electron micrograph of PKHJ–PDMS graft copolymer, 4L (PDMS content $\approx 10\%$, PDMS $\bar{M}_n \approx 3000\,\mathrm{g\,mol^{-1}}$). Magnification: ×234 400

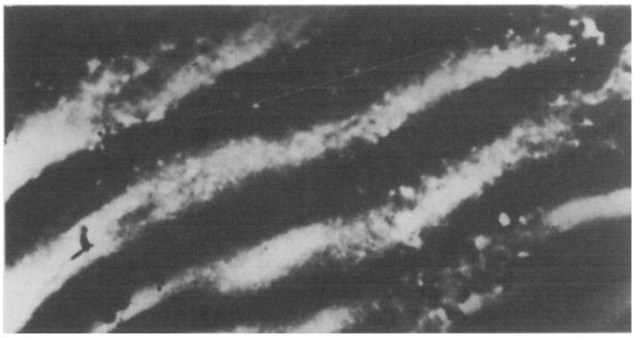


Figure 7 Transmission electron micrograph of PKHJ–PDMS graft copolymer, 4I (PDMS content $\approx 50\%$, PDMS $\bar{M}_n \approx 3000\,\mathrm{g\,mol^{-1}}$). Magnification: ×4400

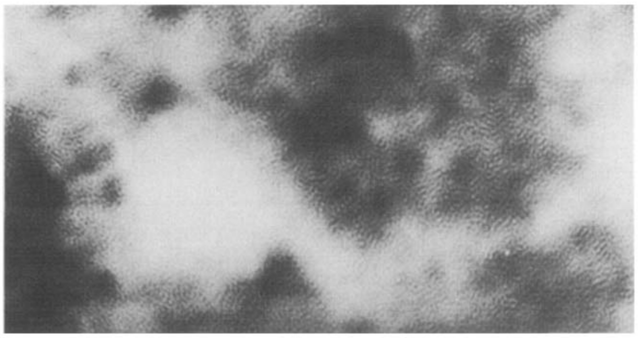


Figure 8 Transmission electron micrograph of PKHJ–PDMS graft copolymer, 4I (PDMS content $\approx 50\%$, PDMS $\bar{M}_n \approx 3000\,\mathrm{g\,mol^{-1}}$). Magnification: ×69 500

measures, the sections still tended to fold and compress during sectioning. This accounts for many of the dark bands observed in the micrographs. *Figures 7* and *8* show typical electron micrographs of 4I (≈50% PDMS). The excellent contrast between phenoxy and PDMS is exemplified in this case. At low magnifications, a well defined lamellar structure is apparent. This structure is definitely a real effect, since it is deformed around voids but random in orientation elsewhere. The interdomain spacing for the phenoxy phase was estimated to be in the region of ≈50 Å and that for the PDMS domains to be ≈40 Å. Once again, at higher magnifications fine structure is evident across the whole material irrespective of dark or light regions. This effect is similar to that descriged above and at this level of magnification, these features may represent actual molecular shapes.

CONCLUSIONS

Polyhydroxyether–PDMS graft copolymers were subjected to detailed analysis to determine the effects of factors such as the $\bar{M}_n$ of the PDMS segments, overall PDMS content and nature of the graft linkage on thermal characteristics, hydrolytic stability, tensile properties and morphology. The optical and thermal characteristics of the copolymers were consistent with a microphase separated morphology. TEM studies revealed a characteristic lamellar type structure at intermediate compositions. At low PDMS concentrations, no significant heterophase domains were observed. The poor tensile elongation exhibited at this composition level appeared to be a direct consequence of the lack of significant PDMS domains. Thermal stability measurements indicated that the copolymers were unsuitable for the preparation of PES blends by melt processing. However, there is considerable scope for improving the thermo-oxidative stability through structural variations in the phenoxy backbone or the PDMS side chains.

ACKNOWLEDGEMENTS

The authors wish to thank ICI for the financial support of this research. Helpful discussions with S. Rostami (ICI) and J. Bilton (Imperial College) are gratefully acknowledged.

REFERENCES

1 Holohan, A. T., George, M. H., Barrie, J. A. and Parker, D. G. *Polymer* 1992, **33**, 852

2 Bajaj, P. and Varshney, S. K. *Polymer* 1980, **21**, 201

3 Varshney, S. K., Beatty, C. L. and Bajaj, P. *Polym. Prepr.* 1981, **22**, 321

4 Holohan, A. T. *PhD Thesis* University of London, 1991

5 Cameron, G. G. and Chisholm, M. S. *Polymer* 1986, **27**, 437

6 Tyagi, D., McGrath, J. E. and Wilkes, G. L. *Polym. Eng. Sci.* 1986, **26**, 1371

7 Noshay, A., Matzner, M. and Merriam, C. N. *J. Polym. Sci., Polym. Chem. Edn* 1971, **9**, 3147

8 Wheatley, G. W. *PhD Thesis* Humberside College of Higher Education, 1988

9 Morris, M. *PhD Thesis* Sheffield City Polytechnic, 1988

10 Nagase, Y., Naruse, A. and Matsui, K. *Polymer* 1989, **68**, 1931

11 Noshay, A. and McGrath, J. E. 'Block Copolymers—Overview and Critical Survey', Academic Press, New York, 1977

12 Allport, D. C. and Janes, W. H. (Eds) 'Block Copolymers', Applied Science, London, 1973

13 McGrath, J. E. *Pure Appl. Chem.* 1983, **55**, 1573

14 Aggarwal, S. L. (Ed.) 'Block Copolymers', Plenum Press, New York, 1970

15 Tyagi, D. *PhD Thesis* Virginia Polytechnic Institute and State University, Blacksburg, 1985