Polyhydroxyether–polydimethylsiloxane graft copolymers: 1. Synthesis and characterization

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

and David G. Parker
ICI Advanced Materials, Wilton, Cleveland TS6 8JE, UK
(Received 18 November 1990; accepted in revised form 4 March 1991)

Graft copolymers of a bisphenol-A-based polyhydroxyether (phenoxy) and polydimethylsiloxane (PDMS) were prepared by (1) the reaction of phenoxy and chlorosilyl-terminated PDMS, and (2) the heterogeneous Pt-catalysed hydrosilation of allyl-derivatized phenoxy with hydrosilyl-terminated PDMS. The monofunctional PDMS oligomers were prepared by the anionic polymerization of hexamethylcyclotrisiloxane (D_3) using *n*-BuLi as initiator and chlorodimethylsilane (CDMS) or dichlorodimethylsilane (DCDMS) as terminating agent. The copolymers were characterized by ^{1}H and ^{13}C n.m.r. spectroscopy, gel permeation chromatography (g.p.c.), t.g.a., d.s.c., and i.r. spectroscopy.

(Keywords: polyhydroxyether; polydimethylsiloxane; graft copolymer; hydrosilation; impact modifier)

INTRODUCTION

As an alternative to developing new polymers tailored for specific end uses, which can be very costly, the requirements are being increasingly met by the blending or copolymerization of existing materials, or a combination of both. The blending of two homopolymers is often complicated by the immiscibility of the two components, resulting in poor interfacial adhesion and very poor mechanical properties. Miscible blends of amorphous polymers are rare and are normally characterized by single-phase morphology. As a result they are transparent and exhibit physical properties intermediate between those of the components. One such system which has been extensively studied is the PES (polyethersulphone)–phenoxy blend[1]. These polymers have been shown to be miscible over the whole range of compositions, resulting mainly from their structural similarities and specific polymer–polymer interactions.

The principal features of PES are its exceptional resistance to creep, outstanding thermo-oxidative stability, rigidity, transparency, and self-extinguishing characteristics. Phenoxy has many properties in common with PES; however, its relatively low softening point ($T_g \approx$ 90°C) has limited its utility. The blends have been investigated mainly for their water sorption[2] and gas transport[3] properties. Although in general the mechanical properties of PES–phenoxy blends would be expected to be volume averages of the properties of the individual components, phenoxy-based copolymer systems present a convenient way of modifying specific properties of PES.

The copolymers described here were synthesized primarily for evaluation as impact modifiers for PES. Rubber modification is one of the oldest and most widely used methods for improving impact resistance. Many variations on the nature of the rubber additive have been developed. Recently the technique of additive blending of block and graft copolymers has received a great deal of attention. Noshay *et al.*[4] report remarkable improvements in the toughness of polysulphone by the addition of as little as 5% polysulphone–PDMS block copolymer.

The inclusion of polysiloxanes in block and graft copolymers has been used with great effect to impart desirable properties in a wide range of materials. The application of PDMS graft copolymers in gas separation processes is currently receiving a great deal of attention[5–8]. Polysiloxanes are valued primarily for their outstanding thermo-oxidative stability, low T_g, water repellancy, and high gas permeability. This unique combination of properties, together with the incompatibility of polysiloxanes with most organic polymers, confers useful morphological and surfactive properties on copolymers comprising the two components.

The development of the anionic polymerization of D_3 has made it possible to prepare PDMS oligomers with various reactive end groups for the synthesis of multiphase graft copolymers with well-defined PDMS segments. Of particular interest have been those oligomers which possess terminal functional groups capable of radical polymerization (macromonomers) such as vinyl, styryl and methacrylate groups[7]. However, the wide range of functional groups which can be incorporated into the oligomers has greatly extended their utility in copolymer systems other than those prepared by radical polymerization.

---

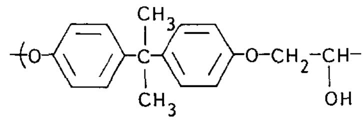
* To whom correspondence should be addressed

0032-3861/92/040852-07

EXPERIMENTAL

*Materials**

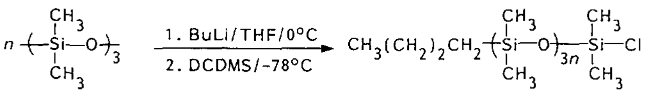
Phenoxy resin (PKHJ) was kindly donated by Union Carbide and used as supplied. It has a quoted density of 1.17 g cm^{-3}, a refractive index of 1.598 and a number-average molecular mass of 30000 g mol^{-1}. Hexamethylcyclotrisiloxane (Rose Chemical) was dried and distilled over calcium hydride. Chlorodimethylsilane and dichlorodimethylsilane were kindly donated by Dow Corning (Europe) and were distilled under argon before use. THF was distilled from the purple Na–benzophenone ketal before use. Chlorobenzene was dried and distilled over phosphorus pentoxide. Chloroform was washed with water, dried over calcium chloride and then refluxed with and fractionally distilled from phosphorus pentoxide before use. Pyridine was refluxed with and fractionally distilled from BaO. DMF was dried and distilled over BaO under reduced pressure. Pt/C (5%), allyl isocyanate, di-*n*-butyltin dilaurate and *n*-BuLi in *n*-hexane were used as supplied.



UCAR PKHJ

Preparation of chlorosilyl-terminated PDMS (PDMS-Cl) oligomers

Scheme 1



PDMS–Cl oligomers were prepared by the anionic polymerization of D_3 using *n*-BuLi as initiator and dichlorodimethylsilane (DCDMS) as terminating agent (*Scheme 1*). The preparation was performed using standard syringe techniques, with all reagent manipulations carried out under argon. A typical procedure was as follows.

A stock solution of D_3 in THF (30 ml, 50% w/v) was transferred to a preflamed and argon-purged one-neck round-bottom flask equipped with a magnetic follower and rubber septum. The flask was immersed in an ice–water bath, and a solution of *n*-BuLi in *n*-hexane (0.018 mol in 11.25 ml) was immediately added with stirring to initiate the polymerization. The polymerization was allowed to proceed at room temperature for 15–20 h until at least 90% conversion had been reached, as determined by g.c. The living anion solution was then added dropwise with stirring at −78°C to DCDMS (0.360 mol) contained in a three-neck round-bottom flask set up for vacuum distillation. The solution was vacuum-stripped while the pot temperature was gradually raised to 100°C to remove excess DCDMS, THF and other volatiles. The LiCl precipitate was removed by filtration.

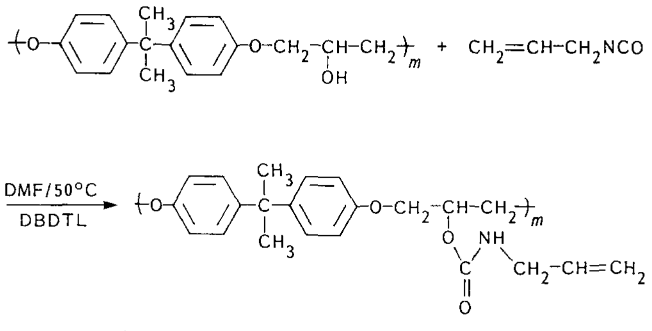
It should be mentioned that chlorosilyl-terminated oligomers have also been prepared using a method similar to that adopted by Nagase *et al.*[5], i.e. hydrosilation of chlorodimethylvinysilane (CDMVS) with hydrosilyl-terminated PDMS. However, in addition to the high cost of this method, low functionalities were obtained (<0.7), primarily as a result of the slow precipitation of colloidal Pt(0) from the oligomers.

Preparation of hydrosilyl-terminated PDMS (PDMS-H) oligomers

PDMS-H oligomers were prepared in a similar manner to PDMS-Cl. However, in this instance the reaction was terminated by the slow addition of chlorodimethylsilane (CDMS) (50% excess) to the living anion solution at −78°C. After removal of the solvent and filtration of the LiCl precipitate, the product was vacuum-dried at 120°C to remove cyclics and other volatiles.

Preparation of allyl-derivatized PKHJ (PKHJ(AL))

Scheme 2

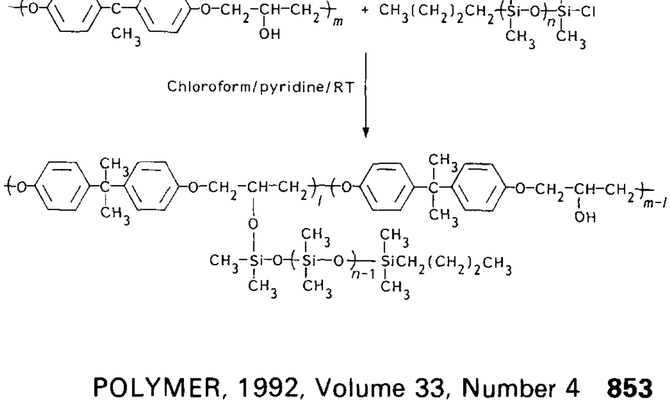


PKHJ(AL) was prepared by the reaction of PKHJ and allyl isocyanate using di-*n*-butyltin dilaurate (DBTDL) as catalyst (*Scheme 2*). PKHJ hydroxyl content was determined using the method described by Lee and Neville[9]. A typical procedure was as follows.

PKHJ (50 g, 0.205 mol OH) was charged into a 1 litre round-bottom flask equipped with a mechanical stirrer, argon inlet tube and dropping funnel. The flask was gently flamed and purged with argon. DMF (40 ml) was added, and after dissolution of PKHJ, 4 drops of DBTDL were added. Allyl isocyanate (20 ml, 0.226 mol, 10% excess) was transferred to a dropping funnel and added slowly with stirring over a period of 15 min. The dropping funnel was replaced with a condenser fitted with a $CaCl_2$ guard tube. The mixture was then heated to 50°C. Stirring was maintained for a further 30 min, and after cooling, the product was isolated by precipitation of the reaction mixture into methanol. The product was then vacuum-dried at 40°C. Further purification was carried out by reprecipitation of a solution of the product in THF into water.

Preparation of Si–O–C-linked PKHJ–PDMS graft copolymers

Scheme 3



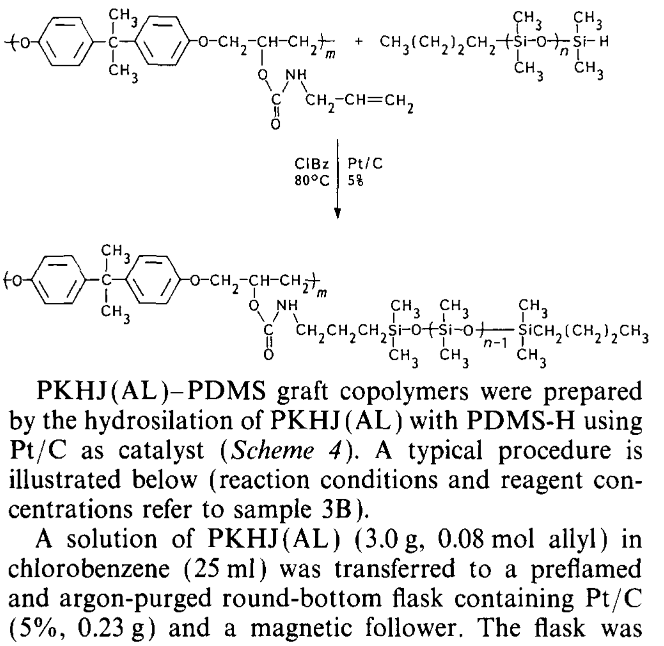
---

* Unless otherwise specified, all materials were supplied by Aldrich Chemical Co.

PKHJ–PDMS graft copolymers were synthesized by the polymer–polymer reaction between PDMS–Cl and PKHJ (*Scheme 3*). Owing to the high reactivity of the terminal silylchloride group, PDMS-Cl oligomers were normally used directly after preparation. A typical synthesis is illustrated in the following example (reaction conditions and reagent concentrations refer to sample 4I). PKHJ (0.7 mol OH) was charged into a three-neck round-bottom flask equipped with a mechanical stirrer, dropping funnel and rubber septum. The flask was gently flamed and purged with argon. $CHCl_3$ was added, and after dissolution of the resin, pyridine (0.028 mol) was syringed into the flask. A solution of PDMS-Cl(4) (0.014 mol Si–Cl) in $CHCl_3$ (50%) was then added dropwise with stirring over a period of 30 min. Stirring was maintained for a further 3 h and the product was isolated by precipitation of the reaction mixture into methanol. After drying, the product was extracted with *n*-hexane*. Further purification was carried out by reprecipitation of a solution of the product in THF into an ice–water mixture.

Preparation of Si–C-linked PKHJ(AL)–PDMS graft copolymers

Scheme 4



PKHJ(AL)–PDMS graft copolymers were prepared by the hydrosilation of PKHJ(AL) with PDMS-H using Pt/C as catalyst (*Scheme 4*). A typical procedure is illustrated below (reaction conditions and reagent concentrations refer to sample 3B).

A solution of PKHJ(AL) (3.0 g, 0.08 mol allyl) in chlorobenzene (25 ml) was transferred to a preflamed and argon-purged round-bottom flask containing Pt/C (5%, 0.23 g) and a magnetic follower. The flask was equipped with a condenser, argon inlet tube and rubber septum. The flask was gently heated to 50°C and a solution of PDMS-H(5) (9.2 g, 0.08 mol Si–H) in chlorobezene (30 ml) was added dropwise with stirring. The mixture was heated to 80°C and stirring was maintained for a further 2 h. Samples were withdrawn periodically for i.r. analysis. After cooling, the reaction mixture was centrifuged to remove the Pt/C catalyst. The supernatant liquid was then filtered and the product was isolated after dilution with $CHCl_3$ by precipitation into methanol. The product was then dried under vacuum at 50°C.

Characterization

^1H and ^{13}C n.m.r. spectra were recorded using a Bruker AM-500 *FT*n.m.r. spectrometer. The spectra were obtained at ambient temperature (≈21°C) using $CDCl_3$ as solvent. G.c. measurements were carried out using a Perkin–Elmer 8402 gas chromatograph equipped with a carbowax 20M capillary column. Average molecular weights and molecular weight distributions were determined by g.p.c. using a mixed 5 μm PL gel column. I.r. spectra were recorded using a Perkin–Elmer 683 infrared spectrophotometer.

RESULTS AND DISCUSSION

Preparation of monofunctional PDMS oligomers

The preparation of PDMS-H oligomers is well documented[5,6], and the methods used in this work were very similar, with some minor modifications. Provided that stringent efforts are made to avoid atmospheric contamination during the synthesis and only ultra-pure reagents are used, the preparations are reproducible and high functionalities can be obtained.

The molecular weight and molecular weight distribution of the oligomers were determined directly by gel permeation chromatography (g.p.c.). A single refractive index (r.i.) detection system was used with reverse polarity output. Toluene was used as the solvent and the instrument was calibrated using polystyrene standards (Polymer Labs). Number-average molecular weights were also estimated by ^1H n.m.r. spectroscopy. The value of $\bar{M}_n$ was calculated from the ratio of the integral of the *n*-butyl protons to that of the main chain dimethylsiloxy protons:

$Si{-}CH_2(CH_2)_2CH_3$ (δ ppm, 0.53, 1.31 and 0.88);

$-Si(CH_3)_2O-$ (δ ppm, 0.10).

The functionality of the oligomers was also determined by ^1H n.m.r. spectroscopy by comparing the *n*-butyl proton integrals with the terminal silane or dimethylsilylchloride proton integrals:

$Si{-}H$ (δ ppm, 4.71); $Si(CH_3)_2Cl$ (δ ppm, 0.45).

The molecular weight and functionality data for a series of PDMS-H oligomers are summarized in *Table 1*.

Figure 1 shows the ^1H n.m.r. spectrum of PDMS-Cl(4) ($\overline{DP} \approx 40$). The spectrum was recorded directly after vacuum stripping and filtration of the oligomer. The signal at 0.45 ppm was assigned to the terminal dimethylsilylchloride group. The complete removal of DCDMS was inferred from the absence of a signal at 0.81 ppm corresponding to the gem dimethyl group.

Preparation of allyl-derivatized PKHJ (PKHJ(AL))

Average molecular weights for PKHJ were determined as polystyrene equivalents by g.p.c. using THF as solvent. Values were corrected using the universal calibration procedure. The Mark–Houwink constants were taken from Iribarren *et al.*[10] The results are summarized below:

$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
27 300	80 100	2.93

The pendant hydroxyl groups in PKHJ allow for extensive modification of the bulk material. Although no detailed study of the reactivity of the hydroxyl groups was made, they undergo many of the reactions characteristic of monomeric secondary hydroxyl groups, e.g. acylation, oxidation. Extensive modifications have been carried out by Reinking *et al.*[11].

---

* Hexane extraction was carried out only when the calculated siloxane content was less than 50%. Previous i.r. studies showed that when the siloxane content exceeded 50% the hexane extracts also contained appreciable quantities (≈2%) of highly grafted PKHJ

In general, the addition of alcohols to isocyanates is very facile, and high yields can be obtained. The use of allyl isocyanate provides a convenient way of introducing pendant unsaturated groups into PKHJ. The reaction approaches completion in 2.5 h in THF at 50°C. As expected, the use of a dipolar aprotic solvent (DMF) considerably reduces the reaction time (<0.5 h). The ^{1}H n.m.r. spectra of PKHJ(AL) and the parent PKHJ are illustrated in *Figure 2* together with proton assignments. Formation of the urethane linkage is accompanied by the loss of the hydroxyl resonance at 2.62 ppm and the appearance of the N–H resonance at 4.87 ppm. This value alters from 4.87 to 7.50 ppm on changing the solvent from $CDCl_3$ to DMSO-d_6. The identity of the N–H resonance was confirmed by proton decoupling. The PKHJ methine resonance is shifted upfield as a result of the increased deshielding effect of the ester moiety. The methylene resonance is similarly affected, but to a lesser extent.

By altering the ratio of [NCO] to [OH], partially modified PKHJ can be obtained with varying allyl content. The sample represented in *Figure 2* is the reaction product obtained using a slight excess of [NCO]. Such products display very poor thermo-oxidative stability resulting in a crosslinked infusible solid. The rate of cure is quite slow at 60°C but becomes significant at temperatures above 120°C. Crosslinking is

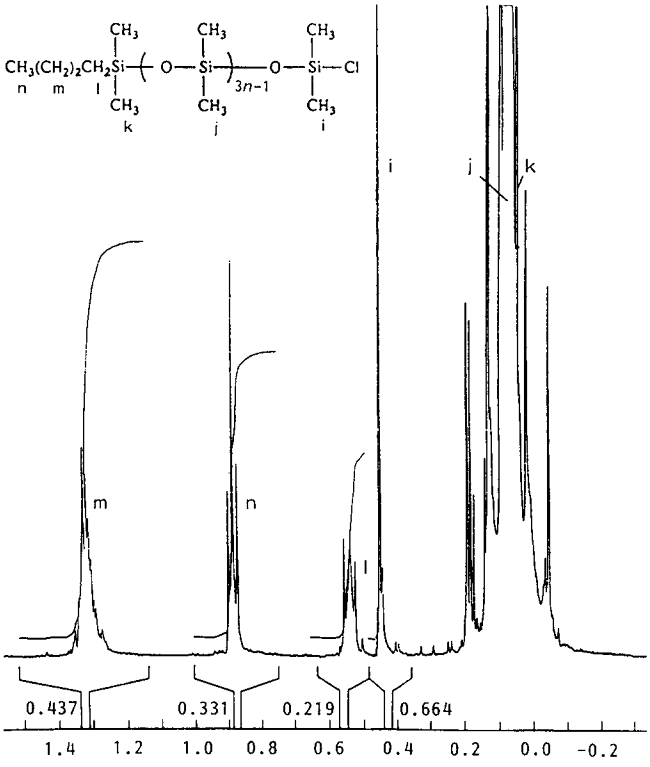


Figure 1 500 mHz ^{1}H n.m.r. spectrum of PDMS-Cl(4) ($\overline{DP} = 40$)

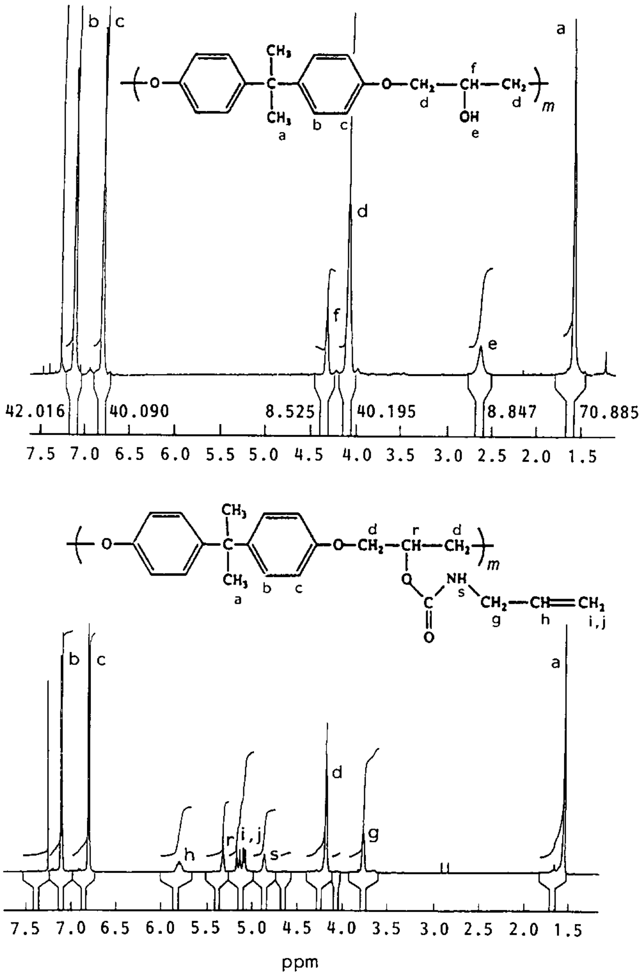


Figure 2 250 mHz ^{1}H n.m.r. spectra of allyl-derivatized PKHJ (PKHJ(AL)) (below) and parent PKHJ (above)

Table 1 Molecular weight and functionality data for a series of PDMS-H oligomers

Sample	PDMS-H(5)	PDMS-H(3)	PDMS-H(4)	PDMS-H(1)
$\bar{M}_n$ (calc.)[a]	1000	2000	4000	15000
$\bar{M}_n$ (g.p.c.)[b]	1350	2200	4800	16900
$\bar{M}_w$ (g.p.c.)[b]	1550	2500	5800	21700
$\bar{M}_w/\bar{M}_n$ (g.p.c.)[b]	1.16	1.13	1.21	1.28
$\bar{M}_n$ (^{1}H n.m.r.)[c]	1150	1900	4100	–
Functionality (^{1}H n.m.r.)[c]	0.98	0.98	0.96	–

[a] Calculated from the equation

$$\bar{M}_n = \frac{D_3(g)}{[n\text{-BuLi}]} + 57\ (\text{RMM of } CH_3(CH_2)_2CH_2\text{–}) + 59\ (\text{or } 93)$$

(59 = RMM of $-Si(CH_3)_2H$; 93 = RMM of $-Si(CH_3)_2Cl$), assuming 100% conversion

[b] Molecular weights as polystyrene equivalents determined by g.p.c.

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

Table 2 Results of the preparation of Si–O–C-linked PKHJ–PDMS graft copolymers

Sample	4E	4F	4G	4H	4I	4J	4K	4L	4M
[Si–Cl]/[OH] (calc.)	1.00	0.50	0.25	0.50	0.15	0.15	0.10	0.01	0.20
$\bar{M}_{nPDMS}$ (calc.)[a]	3000	3000	1000	1000	3000	1000	3000	3000	3000
$\bar{M}_{nPDMS}$ (^1H n.m.r.)[a]	3100	2900	800	900	2800	1000	2500	3100	2700
Average grafting frequency (^1H n.m.r.)[b]	1.00	0.55	0.27	0.50	0.10	0.15	0.12	–	0.23
Siloxane content, % (calc.)[c]	90.0	81.0	45.0	64.8	61.0	35.0	51.0	9.5	68.0
Siloxane content, % (^1H n.m.r.)[d]	91.8	84.7	36.4	60.7	55.7	27.0	42.0	12.0	59.0
Siloxane content, % (i.r.)[e]	93.0	82.0	38.5	62.0	52.0	30.5	43.5	11.5	58.0

[a] See *Table 1*

[b] Calculated using ^1H n.m.r. from the relative reduction in the hydroxyl intensity. Values are quoted as the average number of grafts per repeat unit

[c] Calculated from the equation

$$\text{Siloxane}\ (\%) = \frac{\bar{M}_{nPDMS}}{284(1/G) + \bar{M}_{nPDMS}} \times 100$$

where 284 is the RMM of the PKHJ repeat unit and G is the average grafting frequency

[d] Determined using ^1H n.m.r. from the ratio of the integrals of the respective gem-dimethyl groups of the two components

[e] Determined using a standard i.e. calibration curve

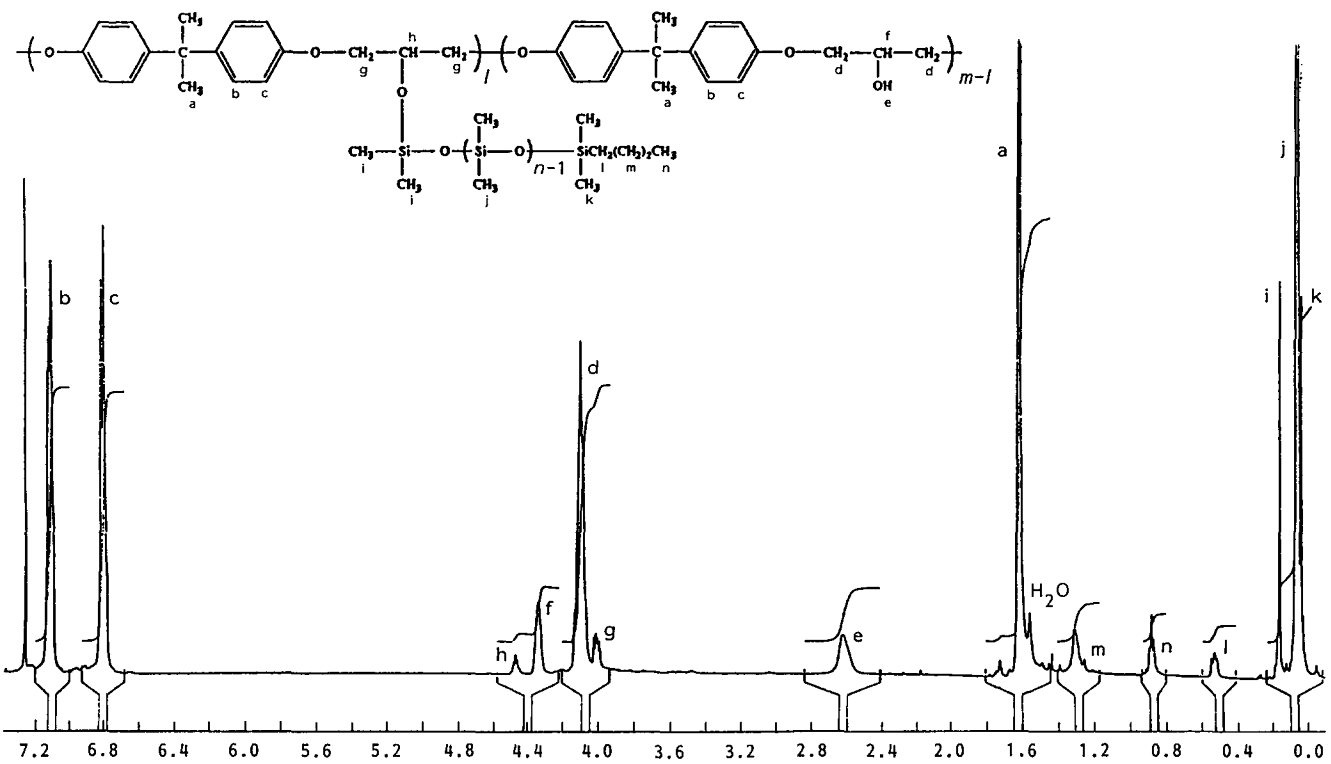


Figure 3 500 mHz ^1H n.m.r. spectrum of PKHJ–PDMS graft copolymer 4I (average siloxane content = 56%, grafting frequency = 0.1)

accompanied by a yellowing of the product and probably proceeds through u.v.-initiated auto-oxidation and Schiff base formation. No apparent anomalies were observed in the d.s.c. or t.g.a. results run in N_2, suggesting that oxidation is integral to this process.

Preparation of Si–O–C-linked PKHJ–PDMS graft copolymers

Although it is widely recognized that the Si–O–C grouping is hydrolytically unstable, the susceptibility to hydrolysis varies greatly, depending on the structure. In 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 the silicon or oxygen atoms increases the rate of hydrolysis. Hydrolytic stability tests are currently being carried out and the results will be published in a subsequent paper.

A series of graft copolymers was prepared with varying siloxane content. The composition was controlled by varying the $\bar{M}_n$ of the PDMS-Cl oligomers or the ratio of [Si–Cl] to [OH]. Copolymer composition was determined using ^1H n.m.r. and i.r. In the former, the relative proportions of the two components were calculated from the ratio of the integral values of their respective gem-dimethyl groups. I.r. determination was carried out by constructing a calibration curve from standard solutions of PKHJ–PDMS mixtures in $CHCl_3$. These results are summarized in *Table 2*.

Figure 3 shows a typical ^1H n.m.r. spectrum of a PKHJ–PDMS graft copolymer together with proton assignments. In addition to the characteristic proton resonances of the parent homopolymers, there are a number of distinct changes which accompany graft copolymerization. As well as the relative reduction in hydroxyl intensity, two sets of methine and methylene proton resonances are observed between 3.9 and 4.6 ppm corresponding to the grafted and ungrafted backbone. This is also evidenced in the ^{13}C n.m.r. spectrum. The relationship between these signals was confirmed using conventional proton decoupling and $^1H-^1H$ correlation spectroscopy (COSY). The methylene attached to the grafted backbone actually give rise to two distinct signals, i.e. 4.0 and 4.1 ppm. However, the latter is obscured by the signal corresponding to the methylene resonance of the ungrafted backbone. The hydrolysis of the terminal silyldimethylchloride group gives rise to an upfield shift of the substituent methyl proton resonance. The signal appears as a sharp singlet at 0.19 ppm.

Typical g.p.c. chromatograms of the parent PKHJ and PDMS homopolymers and the corresponding graft copolymer are presented in *Figure 4*. One of the main problems encountered when analysing copolymers of this type using conventional r.i. or u.v. detection systems is the large difference in response factors of the two components. Ideally the response factors of the homopolymers in both detectors must be calibrated. The compositional heterogeneity of the bulk copolymer is then determined using dual r.i.–u.v. detection. Initial g.p.c. measurements carried out using THF as solvent showed some unusual results. Even as the grafting

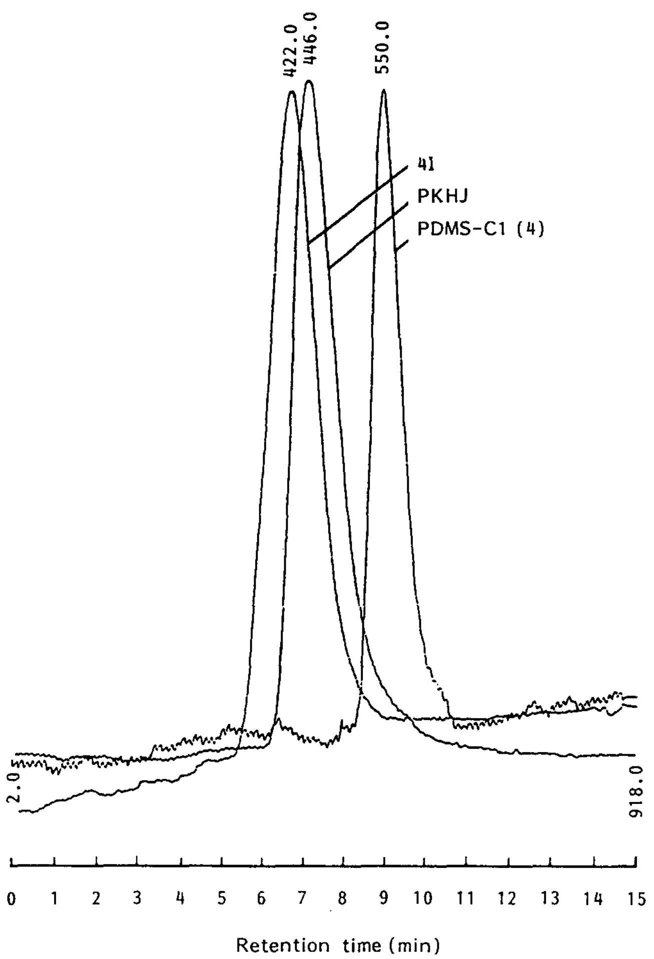


Figure 4 Comparison of g.p.c. traces of PKHJ, 4I and methoxy-derivatized PDMS-Cl(4)

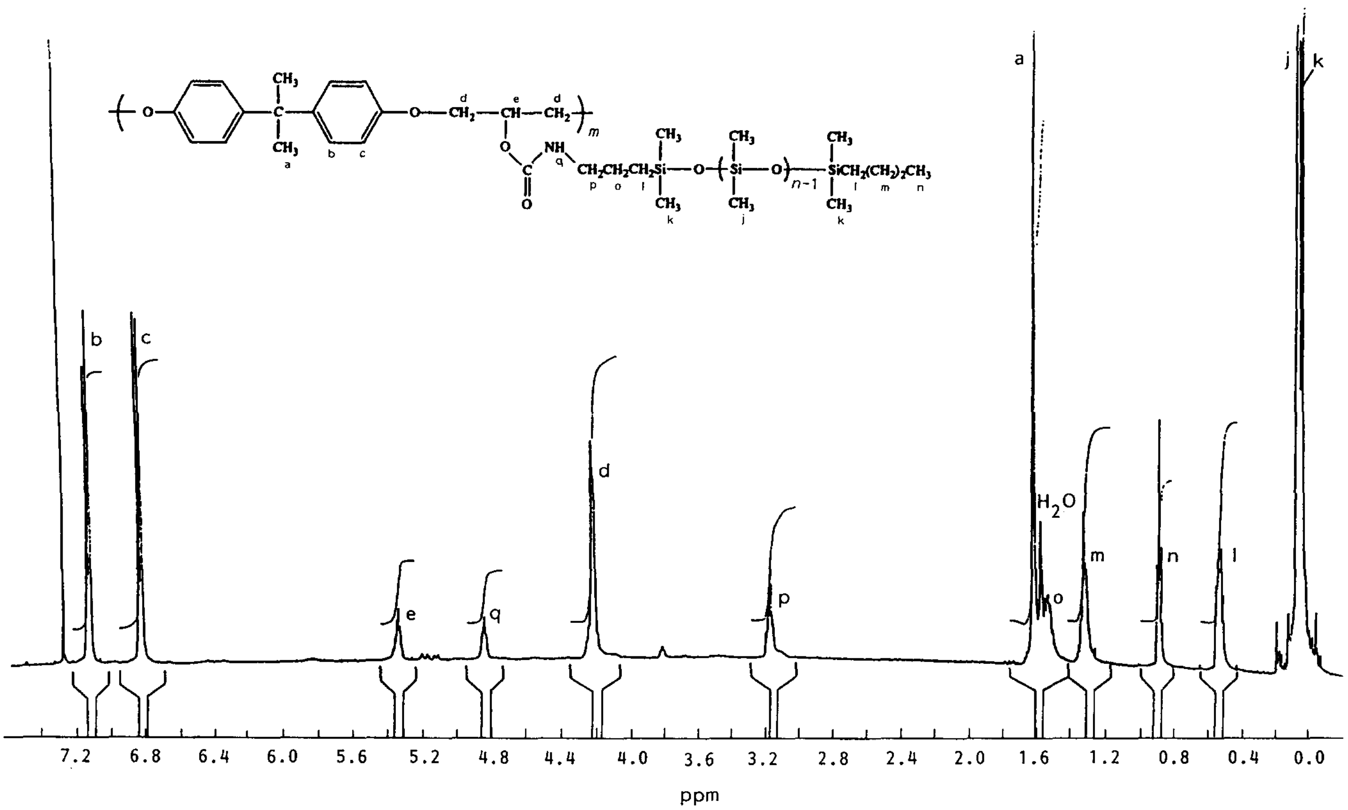


Figure 5 500 mHz ^1H n.m.r. spectrum of PKHJ(AL)–PDMS graft copolymer 3B (average siloxane content = 70%, grafting frequency = 0.95)

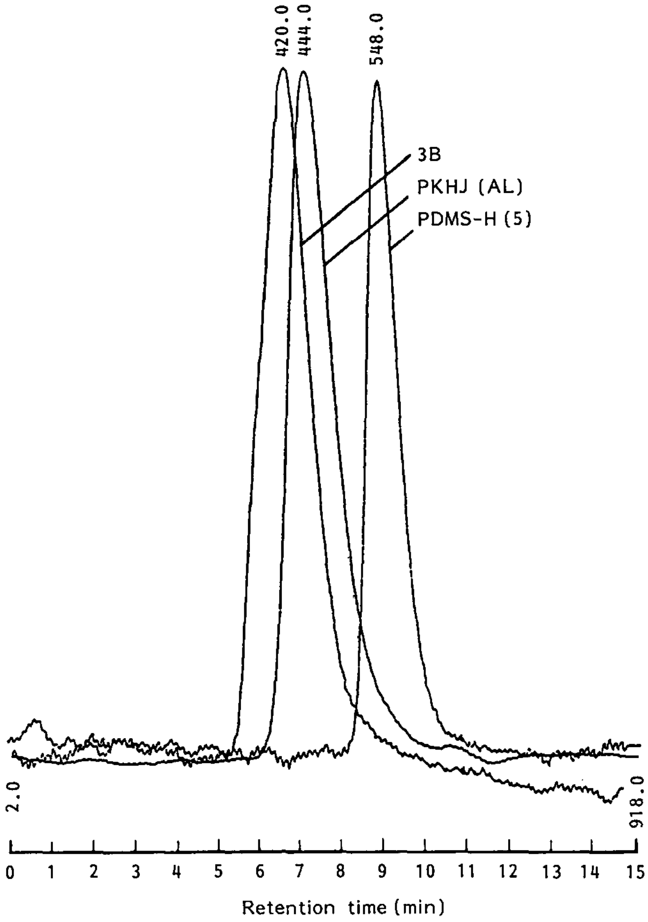


Figure 6 Comparison of g.p.c. traces of PKHJ(AL), 3B and PDMS-H(5)

frequency approached unity (as determined by ^{1}H n.m.r.), the corresponding chromatogram appeared as a modal distribution with a high-molecular-weight shoulder. The retention time of the main peak was identical to that of PKHJ. This was obviously due to the problems mentioned above. In order to obtain a better representation of the actual composition, a mixed solvent system of acetone and THF (60:40) was employed. Although the relative response factor for PDMS in the refractometer was thereby improved, it was still substantially lower than that for PKHJ. Therefore these results can only be viewed in relative terms.

*Preparation of Si–*C-linked PKHJ(AL)*–PDMS graft copolymers*

Hydrosilation is one of the principal methods for the preparation of Si–C bonds and has been used extensively in the synthesis of PDMS block[12–15] and graft[6,16] copolymers. The technique was employed primarily as a result of the improved hydrolytic stability conferred on the graft linkage. Previous attempts where 'homogeneous' catalysis was employed were complicated during isolation of the product by the entrapment of the colloidal Pt by-product in the polymer matrix. However, this problem was eliminated by the use of Pt/C. This is a very effective catalyst for the reaction and is easily removed from a solution of the product by centrifugation. On the basis of the Si–H absorbance band (i.r.), the reaction is >90% complete after 2 h in chlorobenzene at 80°C.

The ^{1}H n.m.r. spectrum of PKHJ(AL)–PDMS 3B is illustrated in *Figure 5* together with proton assignments. Comparison of the spectrum with that of the parent PKHJ(AL) shows that there is still a trace amount of ungrafted backbone. The major changes in the spectrum result from the loss of the silane (δ ppm, 4.71) and olefinic (δ ppm, 5.0–6.0) proton resonances. The signals of particular interest are associated with the newly formed graft linkage. The terminal silylmethylene groups are chemically equivalent and give rise to a complex multiplet at 0.55 ppm. The resonance associated with the methylene protons, p, which were previously deshielded by the olefinic moiety is shifted upfield and appears as a multiplet at 3.16 ppm. The signal corresponding to the intermediate methylene protons, o, centred at 1.53 ppm, is obscured by the PKHJ gem-dimethyl proton resonance.

^{1}H n.m.r. spectroscopy was also used to determine copolymer composition, as described earlier. Once again, g.p.c. analysis was carried out using a mixed acetone–THF (60:40) solvent system. G.p.c. chromatograms of the parent homopolymers and the corresponding graft copolymer are presented in *Figure 6*. Films of the graft copolymer cast from THF solutions (20% w/v) are transparent, indicating microphase separation.

The morphological and mechanical properties of the graft copolymers and blends of the graft copolymers with PES are currently under investigation and will be the subject of a future paper.

ACKNOWLEDGEMENTS

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

REFERENCES

1 Singh, V. B. and Walsh, D. J. *J. Macromol. Sci. Phys.* 1986, **B25**, 65
2 Sagoo, E. S., Barrie, J. A., Swinyard, B. T. and Ash, R. *J. Appl. Polym. Sci.* (in press)
3 Hundal, H. Ph.D. Thesis, University of London, 1990
4 Noshay, A., Matzner, M., Barth, P. B. and Walton, R. K. *Am. Chem. Soc., Div. Org. Coatings Plast. Chem. Preprints* 1974, 217
5 Nagase, Y., Ochiai, J. and Matsui, K. *Polym. Commun.* 1988, **29**, 10
6 Nagase, Y., Naruse, A. and Matsui, K. *Polymer* 1989, **60**, 1931
7 Kawakami, Y., Miki, Y., Tsuda, T., Murthy, R. and Yamashita, Y. *Polym. J.* 1982, **14**, 913
8 Hoover, J., Smith, S., DeSimone, J., Ward, T. and McGrath, J. *Polym. Preprints* 1987, **28**, 390
9 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, 1967
10 Iribarren, J., Iriarte, M., Uriarte, C. and Uruin, J. *J. Appl. Polym. Sci.* 1989, **37**, 3459
11 Reinking, N., Barnabeo, A. and Hale, W. *J. Appl. Polym. Sci.* 1963, 7, 2153
12 Torres, G., Madec, P. and Marechal, E. *Makromol. Chem.* 1989, **190**, 203
13 Haluska, L. US Pat. 2,868,824, 1959
14 Matzer, M. and Noshay, A. US Pat. 3,579,607, 1971
15 Auman, B., Percec, V., Schneider, H. and Cantow, H. *Polymer* 1987, **28**, 1407
16 Chujo, Y., Murai, K. and Yamashita, Y. *Makromol. Chem.* 1985, **186**, 1203