Synthesis and characterization of poly(urethane-*g*-acrylic acid)s

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(*Received 29 March 1988; revised 17 August 1988; accepted 30 September 1988*)

The free-radical copolymerization of a completely hard-block unsaturated polyurethane, based on methylene bis(4-phenylisocyanate), erythrol and butane-1,4-diol, with acrylic acid in the presence of 2,2′-azobisisobutyronitrile at 60°C under various reaction conditions is described. Grafting of poly(acrylic acid) onto the unsaturated polyurethane with pendant alkene groups was shown to be successful. Some of the characteristics of the ungrafted and grafted polyurethane copolymers were studied using microanalysis, gel permeation chromatography (g.p.c.), nuclear magnetic resonance, infra-red spectroscopy and differential scanning calorimetry. The resultant poly(urethane-*g*-acrylic acid)s, poly(U-*g*-AA)s, and the original unsaturated polyurethane were also studied viscometrically in a mixture of tetrahydrofuran and dimethylformamide (DMF) over the temperature range 26–56°C. Different-sized particles, formed in a solution of graft copolymer in water or DMF, were confirmed by photocorrelation scattering. These measurements indicated that predominantly two types of particle were present in both solutions, and values of the hydrodynamic radii and diffusion coefficients were obtained. The number-average molecular weights $\bar{M}_n$ and weight-average molecular weights $\bar{M}_w$ of the polyurethanes and poly(U-*g*-AA)s were determined by g.p.c. relative to polystyrene as a standard. Equilibrium water sorption measurements of the ungrafted polyurethanes were also carried out at room temperature.

(Keywords: polyurethane; poly(acrylic acid); grafting; poly(urethane-*g*-acrylic acid))

INTRODUCTION

Many segmented urethane and urea–urethane copolymers represent important thermoplastic elastomers of the alternating block copolymer type[1]. They are amorphous and the soft block usually has a lower glass transition temperature T_g than the hard blocks, normally formed from the reaction of diols or diamines with the diisocyanate[2]. The wide variation in structure and composition which is possible in urethane polymers makes them excellent candidates for applications as elastomers, fibres, foamed structures and adhesives. Polyurethanes can contain a high concentration of polar groups, in particular the urethane groups resulting from isocyanate–hydroxyl reactions, as well as ester, urea and other groups. The interactions between these polar entities are of great importance in determining the properties of polyurethanes of all types, and especially the polyurethane block copolymers where local concentrations of polar groups occur together, and cause phase separation[1–3].

Conventional immobilization of enzymes in many polymers has been widely carried out[4] but little work has been done with poyurethanes. As part of a wider study of the interaction of enzymes with modified polyurethanes, we have first studied in detail the radical grafting of acrylic acid onto an unsaturated polyurethane. The effects of different reaction times on grafting are reported in this paper.

The original unsaturated polyurethane and the grafted polymers, poly(urethane-*g*-acrylic acid)s, poly(U-*g*-AA)s, were characterized using microanalysis, gel permeation chromatography (g.p.c.), nuclear magnetic resonance (n.m.r.), infra-red (i.r.) spectroscopy and differential scanning calorimetry (d.s.c.). The viscosity behaviour of the unsaturated and grafted polyurethanes in mixtures of tetrahydrofuran (THF) and dimethylformamide (DMF) was also studied, over the temperature range 26–56°C. Some photocorrelation scattering results are also briefly reported in this paper.

EXPERIMENTAL

Materials

Dimethylsulphoxide (DMSO) (Hopkin and Williams) was purified by first drying with Linde molecular sieves, type 3A and 5A, for 24 h followed by barium oxide for another 24 h. The dried DMSO was then fractionally distilled under nitrogen at reduced pressure.

Butane-1,4-diol (BD) (BDH Chemicals) was dried with Linde molecular sieves, 3A and 5A, and then fractionally distilled under nitrogen at reduced pressure.

Methylene bis(4-phenylisocyanate) (MDI) (Bayer UK Ltd) was purified by fractional distillation using a jacketed Vigreux column under nitrogen at reduced pressure to give a white crystalline solid (m.p. 38°C).

Tetrahydrofuran (THF) (BDH Chemicals) was purified by distillation.

Methods

The n.m.r. spectra of all copolymers of interest containing tetramethylsilane (TMS) as an internal standard reference were recorded in deuterated dimethylsulphoxide, using a Bruker WM250 MHz n.m.r. spectrometer.

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Infra-red (i.r.) spectra of the polymers were recorded on a Perkin–Elmer Model 457 Grating Infra-red spectrometer using a thin film of the polymer, cast from THF or DMF solution on a NaCl plate. Equilibrium water sorption measurements were carried out by a method similar to that of Illinger and Schneider[5] by immersing preweighed samples of polymer film in distilled water maintained in a water bath at 30°C.

Preparation of erythrol (ER)

The method of Bissinger *et al.*[6] was used and the erythrol ($CH_2{=}CHCH(OH)CH_2OH$) was finally isolated by distillation under reduced pressure. Finally it was dried over Linde molecular sieves, type 5A and 3A, for a week, and a thin-layer chromatograph (t.l.c.) using ethanol confirmed its purity. It was then characterized by i.r., n.m.r. and microanalysis. The R_f value of erythrol in ethanol at 25°C was equal to 0.655 using Camlab Ambridge Pre-Coated SIL-G-25 t.l.c. plates.

Distillation of acrylic acid (AA)

The AA ($CH_2{=}CHCOOH$) was distilled at 46°C under reduced pressure. A sample of AA examined by g.p.c. using THF as solvent showed only one peak, and confirmed its purity.

Preparation of poly(acrylic acid) (PAA)

Acrylic acid (AA) freshly distilled (3.032 g, 0.042 mol) was dissolved in THF (50 cm^3) with 2,2′-azobisisobutyronitrile (AIBN) (0.048 g, 2.93×10^{-4} mol) as an initiator in a round-bottomed flask. The solution was degassed with nitrogen for 20 min and it was then refluxed under nitrogen for 30 h. The resulting solution was then evaporated to give PAA, as a white solid, which was dried in a vacuum oven at room temperature.

The PAA was characterized by g.p.c. in DMF, which showed only one peak. When the same experiment was carried out for shorter reaction times, the g.p.c. showed two peaks: one due to PAA (low retention time) and the other due to AA monomer at a higher retention time.

Synthesis of an unsaturated segmented polyurethane (PU) based on ER, MDI and BD

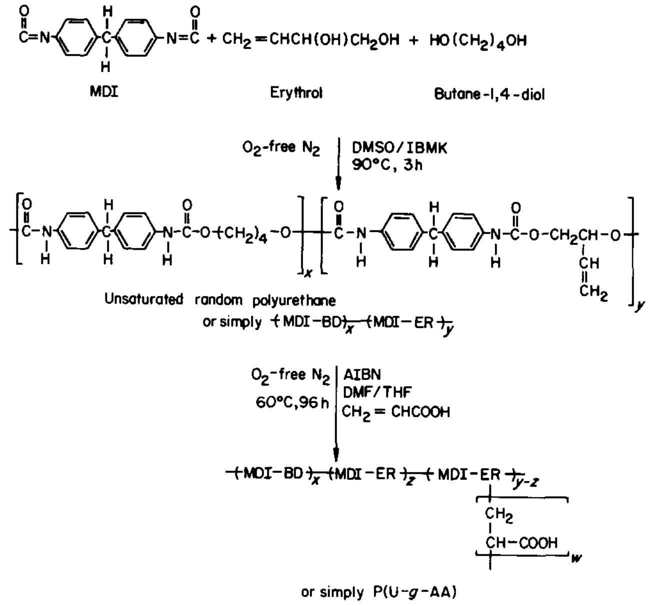
Unsaturated segmented polyurethane copolymers of relatively high and low molecular weight, respectively, were synthesized using methylene bis(4-phenylisocyanate) (MDI), erythrol (ER) and butane-1,4-diol (BD) using the already established method[7–9].

MDI (10.0025 g, 0.039 mol) was first dissolved in isobutyl methyl ketone (IBMK) (10 cm^3). Oxygen-free nitrogen was passed through the mixture slowly while it was stirred, and a mixture of ER (1.766 g, 0.020 mol) and BD (1.8281 g, 0.020 mol) dissolved in DMSO (15 cm^3) was slowly added (30 min) from a dropping funnel. The resulting mixture was stirred at ~90°C for 3 h, cooled and maintained at room temperature for 10 h. The clear solution was then poured into vigorously stirred distilled water (650 cm^3) to precipitate the unsaturated copolymer. The white solid was filtered off and dried in a vacuum oven at room temperature. A reaction time of 3 h at 90°C, as described above, gave a high-molecular-weight copolymer, whereas a reaction time of 1.5 h gave a lower-molecular-weight copolymer, as expected.

Both the high- and low-molecular-weight polyurethanes (PU1 and PU2 respectively) were subsequently used for a radical grafting study with AA. Most of the research was performed using the higher-molecular-weight polyurethane (PU1) and its subsequent radical grafting with AA is described in the next section.

Graft polymerization by radical initiation

Unsaturated copolymer (PU1) (7.84 g) was dissolved in a mixture of DMF/THF (1:1 v/v) (100 cm^3) and placed in a three-necked flask fitted with a N_2 inlet, a pressure-equalizing dropping funnel and a water condenser. The copolymer solution was first degassed for 60 min using O_2-free N_2 and then heated to 60°C under O_2-free N_2. Then a degassed solution of freshly distilled acrylic acid (6.28 g, 0.0872 mol), AIBN (0.086 g, 0.00052 mol) in DMF/THF mixture (1:1 v/v) (20 cm^3) was added slowly dropwise (4 h) to the refluxing copolymer solution. The graft polymerization was continued for 4 days (96 h). The clear solution was cooled to room temperature and poured into vigorously stirred IBMK solution (150 cm^3). The white sticky precipitate was filtered off, washed with fresh IBMK and dried in a vacuum oven at room temperature to give a solid (S). The latter was shown to be P(U-*g*-AA), largely on the basis of g.p.c., n.m.r. and viscosity measurements.



Viscometry

The limiting viscosity number (intrinsic viscosity) of the unsaturated polyurethane, PU1, and the corresponding graft copolymer, poly(U-*g*-AA), was measured using an Ubbelohde viscometer[10,11] in THF, DMF and DMF/THF mixtures of different ratios.

The specific viscosity η_{sp} and the inherent viscosity $\eta_{inh} = (\ln \eta_{rel})/c$ were determined in the usual way. Graphs of η_{sp}/c and η_{inh} against c were plotted and the mean intercept of the two lines at $c = 0$ gave the limiting viscosity number $[\eta]$.

Differential scanning calorimetry

The samples of polyurethane (PU) and of polyurethane grafted with acrylic acid (P(U-*g*-AA)) were analysed using a DuPont-900 Thermal Analyser fitted with a differential scanning calorimetry (d.s.c.) cell. The samples were

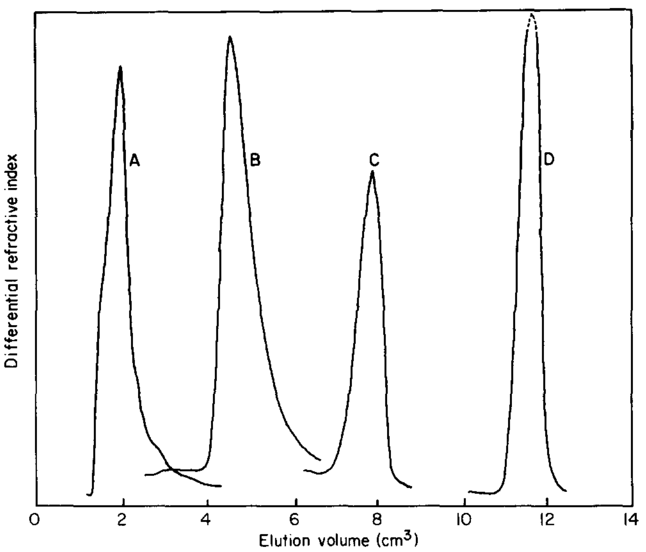


Figure 1 G.p.c. traces of (A) poly(urethane-*g*-acrylic acid) (P(U-*g*-AA)), (B) the original unsaturated polyurethane (PU1), (C) poly(acrylic acid) (PAA) and (D) acrylic acid monomer (AA)

previously dried in a vacuum oven for 2 months at room temperature. Analysis was carried out at a heating rate of 10°C min^{-1} with an empty pan as reference.

Photocorrelation scattering

The photocorrelation instrument used was a Malvern 4700 Series machine, with 128 channels, Spectrophysics 125, using a 1 W argon ion laser at 514.5 nm. The scattering was at 90°, and a cumulant computer analysis was used.

This part of the work was carried out in the Physics Department, Port Sunlight Laboratories of Unilever Research Ltd.

RESULTS AND DISCUSSION

Glass transition temperature

The glass transition temperature T_g of the unsaturated polyurethane, PU1, and its corresponding graft copolymer, P(U-*g*-AA), were assigned as 78 and 59°C, respectively. This may imply some partial miscibility of the two polymer components of the P(U-*g*-AA).

It was observed that when polymer samples were allowed to cool to room temperature and then reheated, the T_g values remained constant, suggesting an absence of thermal degradation[12,13].

Gel permeation chromatography

The g.p.c. trace of a solution of the solid (S) in DMF showed only one peak with a retention time of 90 s less than that of the ungrafted polyurethane. This suggests strongly that S was the graft polymer, P(U-*g*-AA), uncontaminated with unsaturated polyurethane (PU1), PAA or unreacted AA. Typical g.p.c. results are shown in *Figure 1*, where peak A represents P(U-*g*-AA). For comparison, separate samples of unreacted PU, PAA and AA were injected and gave peaks B, C and D, respectively. The grafted polyurethane molecules are eluted first from the g.p.c. column (curve A, *Figure 1*) due to their relative high molecular weights. The positions of the peaks shown in *Figure 1* are as expected from their relative molecular weights, P(U-*g*-AA) > PU1 > PAA > AA, in terms of increasing elution volume.

Average molecular weights

The number-average $\bar{M}_n$ and weight-average $\bar{M}_w$ molecular weights of the unsaturated polyurethane (PU) and of the P(U-*g*-AA) formed under various experimental conditions are shown in *Table 1*. The molecular weights of the P(U-*g*-AA)s are based on g.p.c., using polystyrene standards, and are thus not absolute values.

Increase in the reaction time of synthesis is accompanied by an increase in average molecular weights, as expected, since an increase in grafting, caused by longer reaction times, results in increased molecular weights.

Effect of reaction time on percentage of grafting

The variation in the percentage of grafting with reaction time from 12.5 h to 96 h treatment at 60°C using an initiator, AIBN, was determined, in a mixture of DMF/THF (1:1 v/v), under the same experimental conditions previously described. The difference in the masses of the graft copolymer and the original ungrafted polyurethane, after drying in a vacuum oven at 25°C, were used for this determination using the equation:

$$\text{Grafting (\%)} = \frac{(\text{Mass of P(U-}g\text{-AA)} - \text{Original mass of PU})}{(\text{Original mass of PU})} \times 100$$

A plot of percentage grafting against reaction time is shown in *Figure 2*.

In agreement with results from another system[14], the percentage of grafting increases with reaction time and appears to approach a limiting value. This is probably the result of the depletion of monomer and initiator concentrations, although some shielding of double bonds remaining on the PU may occur due to the existing initially formed poly(acrylic acid) grafts. Thus it was found that the most effective radical grafting took place after a prolonged reaction time (96 h).

Microanalysis

The elemental microanalysis of the polymers (PU1, PU2) and the graft copolymer formed by grafting PU1 for 96 h are shown in *Table 2*. *Figure 2* shows that increasing the grafting time using PU1 causes an increase in the weight per cent grafting and a corresponding decrease in per cent N. The per cent N contents of the graft copolymer samples decrease to give a plateau as the extent of grafting increases. The per cent N results are in good agreement

Table 1 Average molecular weight of polymers from g.p.c. measurements

Polymer[a]	Number-average mol. wt, $\bar{M}_n$	Weight-average mol. wt, $\bar{M}_w$	Reaction time (h)
PU2	1.34×10^5	6.56×10^5	1.5
PU1	1.69×10^5	8.96×10^5	3
P(U-*g*-AA)	1.20×10^6	6.36×10^6	24
P(U-*g*-AA)	1.22×10^6	7.15×10^6	30
P(U-*g*-AA)	1.43×10^6	9.19×10^6	48
P(U-*g*-AA)	1.54×10^6	1.72×10^7	52
P(U-*g*-AA)	1.49×10^6	1.89×10^7	96

[a] P(U-*g*-AA) = poly(urethane-*g*-acrylic acid); PU2 and PU1 represent two unsaturated polyurethanes, described in the text

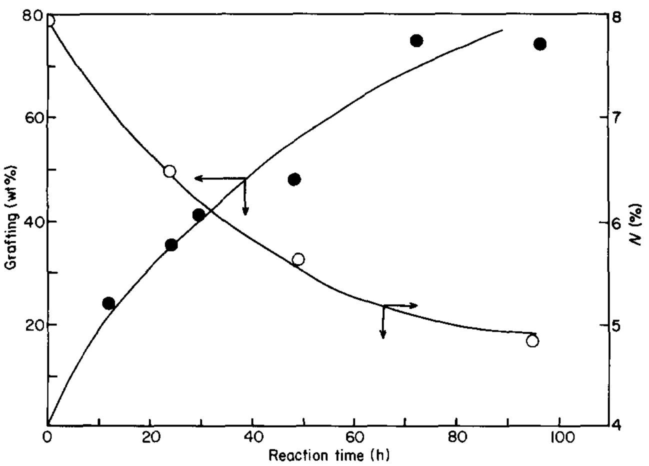


Figure 2 Effect of reaction time on percentage of grafting (●) and per cent N content (○). Polymerization between unsaturated polyurethane (PU1) and acrylic acid (AA) in the presence of initiator (2,2′-azobisisobutyronitrile) in DMF/THF (1:1 v/v) mixture. Reaction temperature 60°C

with the known per cent N value for PU1 of 8.28, as shown in *Table 2*.

Photocorrelation scattering

Photocorrelation scattering (PCS) was carried out using a sample of P(U-*g*-AA) prepared by graft copolymerization for 96 h in a THF/DMF mixture as previously described. The resultant dry polymer was shaken with distilled water and then filtered to give a hazy aqueous solution. Examination by PCS of this aqueous solution at 25°C revealed the existence of two types of particle[15], one with a hydrodynamic radius and diffusion coefficient of 1.81×10^2 Å and $3.02\times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ and another with corresponding values of 1.84×10^2 Å and $2.97\times 10^{-11}\,\mathrm{m^2\,s^{-1}}$.

The results may imply the existence in the aqueous phase of highly swollen free molecules of P(U-*g*-AA), made swollen by the poly(acrylic acid) grafts, together with compacted micelles/aggregates.

Average number of double bonds of polymers

The number-average molecular weight $\bar{M}_n$ of the initial unsaturated polyurethane PU1 was 1.69×10^5, while the molecular weight of one sample of the grafted polyurethane P(U-*g*-AA) formed after 96 h was 1.49×10^6.

Now if the structure of the unsaturated PU is written as $(\mathrm{MDI{-}BD{-}MDI{-}ER{-}})_x$ with a repeat molecular weight of 678.75, then for a number-average molecular weight of the PU, $\bar{M}_n(\mathrm{PU})$, the average number of double bonds in the PU initially is given by:

$$x=\frac{1.69\times 10^5}{678.75}=249.0$$

The molecular weight of the grafted polymer (P(U-*g*-AA), $\bar{M}_n(\mathrm{P(U\text{-}}g\mathrm{\text{-}AA)})$, is given by:

$$\bar{M}_n(\mathrm{P(U\text{-}}g\mathrm{\text{-}AA)})=\bar{M}_n(\mathrm{PU})+n\bar{M}_n(\mathrm{PAA}) \qquad (1)$$

where $\bar{M}_n(\mathrm{PAA})$ is the number-average molecular weight of the poly(acrylic acid) grafts, assumed to be the same as that of the homopolymeric PAA, formed under identical conditions, and n is the average number of grafts per original PU molecule. In a separate experiment, the number-average molecular weight of the PAA was found to be 5.70×10^3, under the same experimental conditions as in the grafting experiment. Hence from the data provided:

$$1.49\times 10^6=1.69\times 10^5+n\times 5.70\times 10^3$$

Therefore:

$$n=\frac{1.49\times 10^6-1.69\times 10^5}{5.70\times 10^3}=231.8$$

Since g.p.c. data provide all the number-average molecular weights used in this calculation, and since there are particular errors in estimating the number-average molecular weight of the graft copolymer due to its low elution volume, the final value of n can only be reported as approximate.

Viscosity behaviour in mixed solvents

The variation of limiting viscosity numbers $[\eta]$ with change of DMF–THF composition at various temperatures is shown in *Figure 3* for the P(U-*g*-AA) sample, previously designated S. The P(U-*g*-AA) dissolved much more rapidly in DMF than in THF, as did the original ungrafted PU, which may imply that DMF is the better solvent, thermodynamically. The viscosity results are unusual in that the limiting viscosity results show a minimum at all temperatures at 50% DMF (v/v) in DMF/THF mixtures, except at 56°C. Also the variation of $[\eta]$ at fixed DMF/THF compositions with temperature does not follow a consistent trend. This unusual type of behaviour for P(U-*g*-AA) has also been noticed in certain other graft and block systems which involve micelle/aggregate formation, but other systems exhibit more regular behaviour[16].

For comparison, the variation of $[\eta]$ with composition at a fixed temperature of 26°C is also shown in *Figure 3* for the original PU before grafting. The variation indicates a maximum in $[\eta]$ at about 50% DMF (v/v) in DMF/THF mixtures, in contrast to the minimum shown by the graft copolymers at the same solvent composition. Also $[\eta]$ of the original PU appears to be much higher than that of P(U-*g*-AA) at 26°C over the whole solvent composition range. This is consistent with the formation of micelles/aggregates by the P(U-*g*-AA) since the nominal weight-average molecular weight of P(U-*g*-AA) found by g.p.c. was about 9.19×10^6 compared with that of the original PU which was 8.96×10^5.

Table 2 Microanalysis results of the copolymers[a]

Polymer sample		Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%) by diff.
PU2	Calc.	67.45	5.32	8.28	18.93
	Found	66.71	5.72	7.00	21.18
PU1	Calc.	67.45	5.32	8.28	18.93
	Found	65.45	5.78	8.20	20.57
P(U-*g*-AA)	Found	57.54	5.92	4.72	31.82

[a] (PU-*g*-AA) was a poly(urethane-*g*-acrylic acid) formed by the reaction of the original polyurethane PU1 for 96 h in solution with acrylic acid and initiator, at 90°C. PU2 and PU1 are the unsaturated polyurethanes described in the text

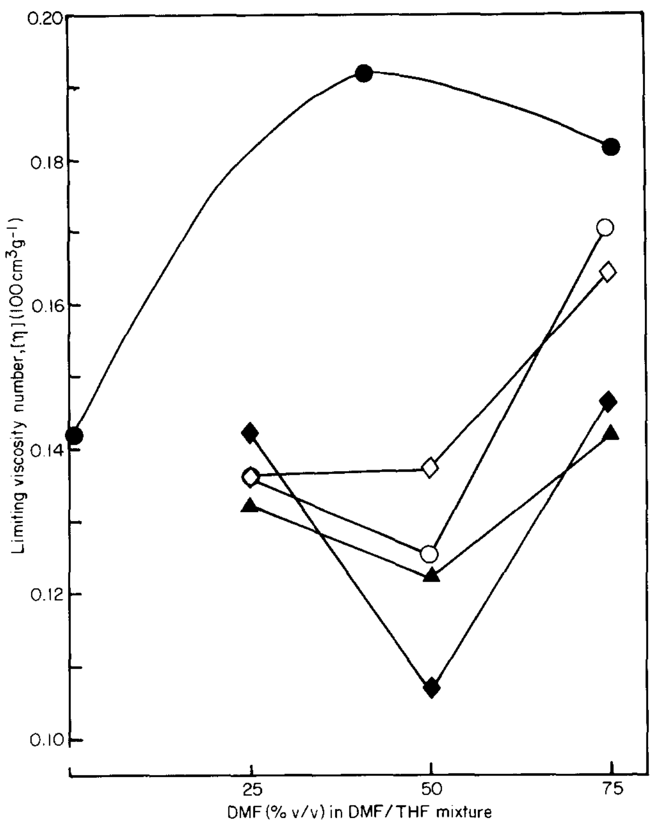


Figure 3 Plots of limiting viscosity number $[\eta]/100\,cm^3\,g^{-1}$ of unsaturated polyurethane (PU1) at a fixed temperature, and of poly(urethane-*g*-acrylic acid) (P(U-*g*-AA)) against percentage volume of DMF in DMF/THF mixtures at various temperatures: unsaturated polyurethane (PU1) (●); P(U-*g*-AA) at (○) 26°C, (▲) 36°C, (◆) 46°C and (◇) 56°C

Water sorption of polyurethane, PU1

When a film of PU1 was immersed in water at 30°C, the equilibrium water uptake only reached 1.7% (w/w) for a period of 12 days. This low value reflects the fact that the polymer only consists of hard blocks.

Infra-red spectroscopy

Figure 4 shows the i.r. spectra of erythrol (*4a*), of polyurethane PU1 (*4b*) and of a P(U-*g*-AA) formed after 48 h (*4c*).

The infra-red spectrum of erythrol (*Figure 4a*) is characteristic of its known structure. For example, there are peaks at 990 and 910 cm^{-1} (s) due to the olefinic C–H out-of-plane bending modes, and further peaks at 1645 cm^{-1} (m), 3025 cm^{-1} (m) and 1880 cm^{-1} (w) also due to the vinyl group. The broad band at about 3020–3550 cm^{-1} (s) is due to the free primary and secondary alcohol groups, possibly with some associated hydroxyl groups. The other peaks are due to C–H and C–C bonds in the molecule.

The spectrum due to PU1 (*Figure 4b*) shows identifiable vinyl-group absorptions at about 990, and 910, 1880 and 3025 cm^{-1}, but all of expected reduced intensity. The peak at 3200–3450 cm^{-1} is due to the N–H stretch of the urethane protons, the peak being broad and intense due to hydrogen bonding[17]. One band at about 3000 cm^{-1} may be due to the C–H stretch of the aromatic groups. The band at about 1650–1750 cm^{-1} due to the urethane carbonyls and the maximum at 1710 cm^{-1} suggest that most of the carbonyl groups are hydrogen-bonded. A strong peak at 1595 cm^{-1} is due to an aromatic C–C stretch. An N–H deformation gave a broad band between 1450 and 1500 cm^{-1}, with the peak at 1410 cm^{-1} due to aliphatic C–H deformations. A band at 1000–1120 cm was attributed to C–O single-bond stretching from the urethane group, and aromatic C–H deformations showed at 850 (w), 820 (s) and 765 (s) cm^{-1}. No sign of unreacted isocyanate was detected as indicated by the absence of a strong peak at about 2250 cm^{-1}.

The spectrum shown in *Figure 4c* for P(U-*g*-AA) shows an overlapping doublet for N–H at 3025–3600 cm^{-1} together with an O–H stretch in COOH of poly(acrylic acid) at 2600–3040 cm^{-1}. The strongly hydrogen-bonded urethane carbonyls appear as a broad band at 1610–1730 cm^{-1} with a maximum at 1680 cm^{-1} and the carbonyls in the PAA units also absorb in these regions. Aromatic C–C stretch and N–H deformation occur around 1590 and 1500 cm^{-1}, respectively. The other peaks are predominantly due to C–H and C–C bonds, with aromatic C–H appearing at 910, 820 and 780 cm^{-1}. The peak due to the vinyl groups at 990 cm^{-1} has disappeared, indicating their depletion, but another peak due to the carbonyls of the poly(acrylic acid) grafts appears at 930 cm^{-1} (s).

Nuclear magnetic resonance spectroscopy

Figure 5 shows the n.m.r. spectra of unsaturated polyurethane PU1 and a sample of the products from the reaction mixture (S, P(U-*g*-AA)). It can be seen from *Figure 5a* that at about 5.8 ppm in the case of ungrafted polyurethane PU1, there is a quartet present, due to unsaturation, whereas in the case of S (*Figure 5b*) this peak is not present, suggesting that radical grafting had taken place to remove unsaturation. Otherwise the n.m.r. spectra were very similar except for the absorptions at 7.05 and 7.35 ppm for sample S.

Further evidence for the saturation of the final grafted polyurethane was shown when this polymer was treated with Br_2 in carbon tetrachloride, when no discoloration

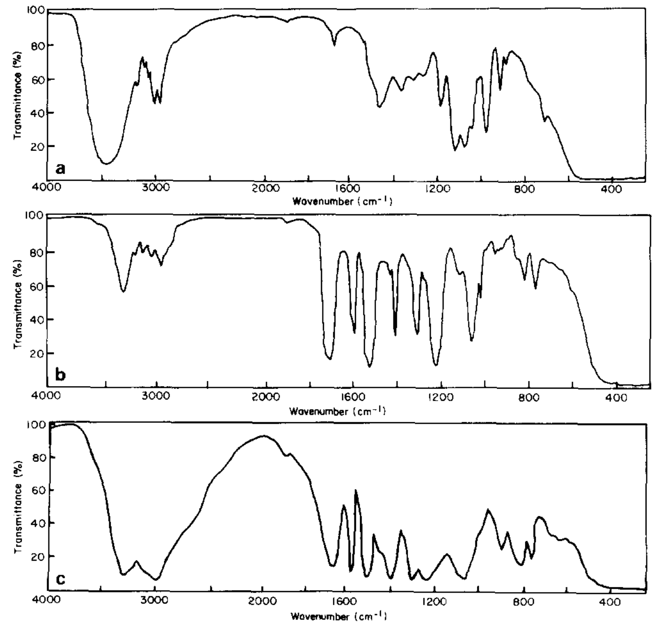


Figure 4 Infra-red spectra of (a) erythrol (ER), (b) original unsaturated polyurethane (PU1) and (c) poly(urethane-*g*-acrylic acid) (P(U-*g*-AA)). Polymer films cast in DMF onto NaCl plates

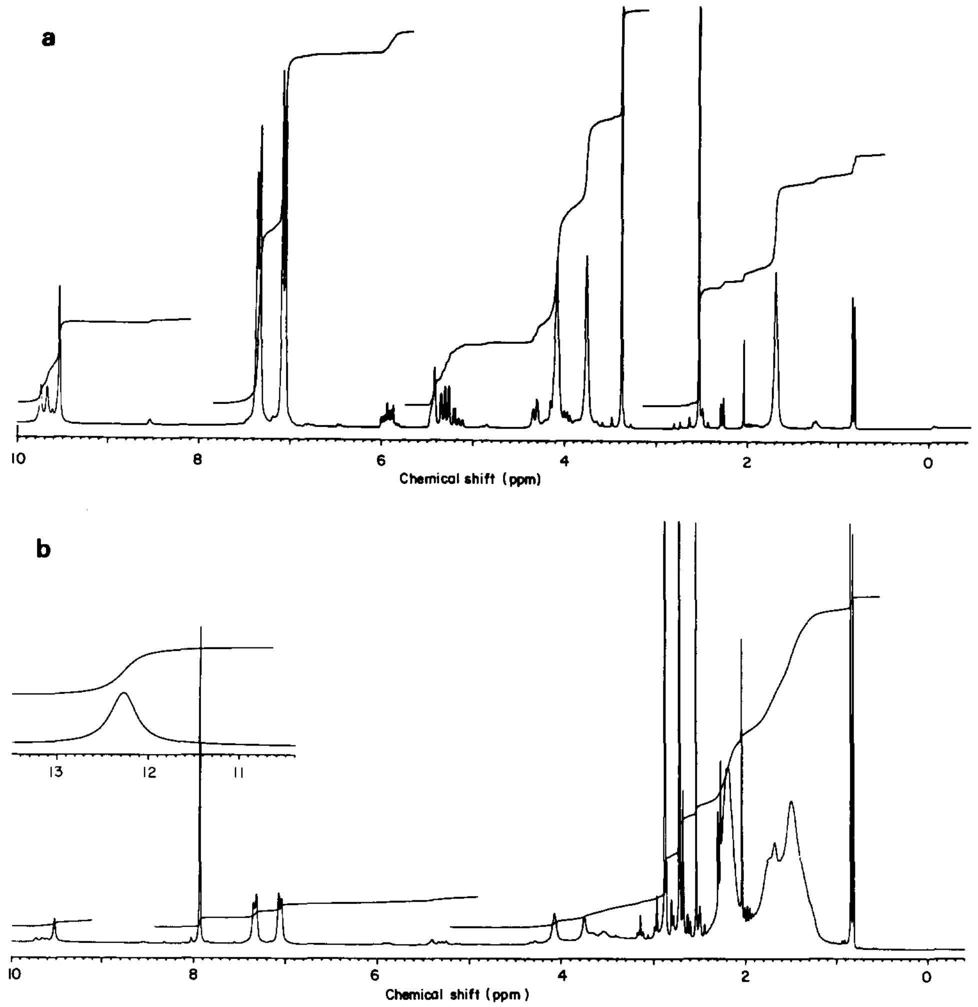


Figure 5 The n.m.r. spectra of (a) original unsaturated polyurethane (PU1) and (b) poly(urethane-*g*-acrylic acid) (P(U-*g*-AA) in dimethylsulphoxide-d_6 ($(CD_3)_2SO$)

occurred. However, in a similar experiment with the unsaturated polymer PU1, discoloration occurred completely within 24 h.

Table 3 Qualitative solubility of unsaturated polyurethane PU1, grafted polyurethane poly(U-*g*-AA), poly(acrylic acid) and acrylic acid at room temperature

	Solubility[a]			
Solvent	PU1	P(U-*g*-AA)	PAA	AA
Water (H_2O)	0	1+0*	1	1
Acetone (CH_3COCH_3)	0	0	0	
Ethanol (C_2H_5OH)	0	0	1	
Ethanol/water (C_2H_5/H_2O) (vol. ratio 1:1)	0	0	1	1
Carbon tetrachloride (CCl_4)	0	0	0	
Chloroform ($CHCl_3$)	0	0	0	
Formamide ($HCONH_2$)	0	0		
Benzene (C_6H_6)	0	0	0	
Toluene (C_7H_8)	0	0	0	
Tetrahydrofuran (C_4H_8O)	1	1	1	1
Diethyl ether ($(C_2H_5)_2O$)	0	0	0	
n-Hexane (C_6H_{12})	0	0	0	
Dimethylsulphoxide ($(CH_3)_2SO$)	1	1	1	
Dimethylformamide ($HCON(CH_3)_2$)	1	1	1	1
Methanol (CH_3OH)	0	0	1	1
Isobutyl methyl ketone (IBMK)	0	0		1

[a] 1 denotes soluble, 0 insoluble at room temperature and 1+0* partially soluble

Solubility

The solubility characteristics of samples of unsaturated polyurethane PU1, P(U-*g*-AA), poly(acrylic acid) and acrylic acid in some solvents are shown in *Table 3*.

CONCLUSIONS

A series of completely hard-block unsaturated polyurethanes has been successfully synthesized, based on methylene bis(4-phenylisocyanate), erythrol and butane-1,4-diol. The unsaturated polyurethanes were grafted radically with acrylic acid monomer in the presence of 2,2′-azobisisobutyronitrile in THF/DMF mixtures at 60°C. The ungrafted polyurethanes and a sample of the separated poly(urethane-*g*-acrylic acid) were characterized using microanalysis, g.p.c. (to give average molecular weights), i.r., n.m.r. and d.s.c. The grafted polyurethane was also studied in aqueous solution by photocorrelation scattering, suggesting that aggregates/micelles were formed at room temperature. Some unusual viscosity data results for the poly(urethane-*g*-acrylic acid) in a mixture of THF/DMF, at 25°C, and also in mixed solvents at different temperatures, 25–60°C, were also presented and compared with the ungrafted unsaturated polyurethane.

ACKNOWLEDGEMENTS

This research was supported by SERC and Unilever Research and involved a Cooperative Award (Award to Dr M. H. George and Dr J. A. Barrie of the Chemistry Department as part of the Imperial College Colloid and Interface Group).

Photocorrelation results were obtained by Dr E. J. Staples working with Dr I. G. Lyle at Unilever Research, Port Sunlight Laboratories.

The authors wish to thank Mr R. N. Sheppard and Mr J. N. Bilton (Chemistry Department, Imperial College) for carrying out the n.m.r. and d.s.c. measurements, for technical advice and for stimulating discussions.

Thanks are also due to Dr K. Hammond (Unilever Research) for helpful discussions during the course of the research.

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