Unsaturated polyurethanes by bulk polymerization and their free radical grafting with acrylic acid

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Relatively high molecular weight unsaturated segmented polyurethanes with pendant double bonds have been synthesized by the bulk polymerization technique using 5-hexene-1,2-diol and 3-allyloxy-1,2-propandiol with butane-1,4-diol as hard segment chain extenders. Two different diisocyanates were investigated: methylene bis(4-cyclohexyl isocyanate), commercially known as Desmodur W, which required a catalyst di-n-butyltin dilaurate, and methylene bis(4-phenyl isocyanate). These unsaturated polyurethanes were grafted with acrylic acid in *N*,*N*-dimethylformamide and tetrahydrofuran using the free radical initiator 2,2-azobisisobutyronitrile. The effect on the graft yield due to variations in the concentrations of acrylic acid, initiator, double bond, soft block polyether and solvent was investigated. The dependence of water and ethanol absorptions upon the degree of grafting and the type of diisocyanate used was also studied.

(Keywords: grafting; polyurethane; unsaturated polyurethane; bulk polymerization; acrylic acid; 5-hexene-1,2-diol; 3-allyloxy-1,2-propandiol)

INTRODUCTION

Graft copolymerization offers the possibility of improving the characteristic properties in conventional copolymers such as their solubility, physicochemical and mechanical properties.

Synthesis of graft polyurethanes by free radical, irradiation and ionic techniques have been reported. Adibi *et al.*[1] reported the ionic grafting of acrylonitrile onto the urethane nitrogen of a segmented polyurethane based on methylene bis(4-phenyl isocyanate) (MDI) by substitution of the hydrogen atom. Unsaturated polyethers, polyesters or butene-1,4-diol incorporated into the backbone of copolymers have provided convenient grafting sites. Jansen *et al.*[2] reported the grafting of 2-hydroxyethyl methacrylate (HEMA) onto polyurethane films using ^{60}Co gamma radiation. Egboh *et al.*[3,4] reported successful grafting with acrylamide, methacrylonitrile, methyl methacrylate, and more recently, HEMA, using 2,2-azobisisobutyronitrile (AIBN) as initiator in *N*,*N*-dimethylformamide (DMF).

The solution copolymerization of unsaturated polyurethanes with short chain pendant double bonds using erythrol (ER), 5-hexene-1,2-diol (HD), and 3-allyloxy-1,2-propandiol (APD) has been reported previously in detail[5]. These pendant double bonds were considered to be more reactive than those in the backbone due to their relatively decreased steric hindrance from the backbone itself.

Unsaturated polyurethanes based on MDI, Desmodur W (DW, hylene W or methylene bis(4-cyclohexyl isocyanate)), and the unsaturated diols HD and APD have been synthesized by the bulk polymerization technique, producing higher molecular weights than previously. Acrylic acid (AA) was grafted onto the double bonds using AIBN as initiator and DMF as solvent. The influence of initiator, monomer, soft segment and double bond concentrations on the graft yield was investigated.

In this paper, we also report some results from water/ethanol uptake experiments. The mechanical properties of the ungrafted and grafted polymers are currently being studied. Traces of DMF retained from the grafting experiments could reduce the suitability of the copolymers as potential biomedical materials and so the more volatile tetrahydrofuran (THF) was investigated as solvent. Since THF was a more volatile solvent, the reaction had to be carried out at lower temperatures.

EXPERIMENTAL

Solvents and reagents

Butane-1,4-diol, BD, (BDH Ltd) was dried over 4 Å (0.4 nm) Linde molecular sieves for 2 weeks, distilled and stored over fresh molecular sieves. Polypropylene glycol 1025, PPG, (MTM Chem. Ltd) was dried over 4 Å Linde molecular sieves for 2 weeks before use. 3-Allyloxy-1,2-propandiol, APD, (Aldrich Chem. Co. Ltd) was dried over 4 Å Linde molecular sieves for 2 d before use. 5-Hexene-1,2-diol, HD, (Aldrich Chem. Co. Ltd) was distilled under reduced pressure and stored over 4 Å Linde molecular sieves. Methylene bis(4-phenyl isocyanate), MDI, (Bayer) was used as supplied. Desmodur W, DW, (Du Pont) was used as supplied. Di-n-butyltin dilaurate, T12, (BDH Ltd) was used as supplied. Acrylic acid, AA, (Aldrich Chem. Co. Ltd) was distilled under reduced pressure and stored at −4°C until required. 2,2′-Azobisisobutyronitrile, AIBN, (BDH Ltd) was recrystallized from methanol and stored at −4°C. Tetrahydrofuran, THF, (BDH Ltd) and *N*,*N*-dimethylformamide, DMF, (Aldrich Chem. Co. Ltd) were distilled and stored over 4 Å Linde molecular sieves. Ethanol, 99.7% (James Burrough Ltd) was used as supplied.

A schematic diagram of the copolymerization and grafting reactions is given in *Scheme 1*.

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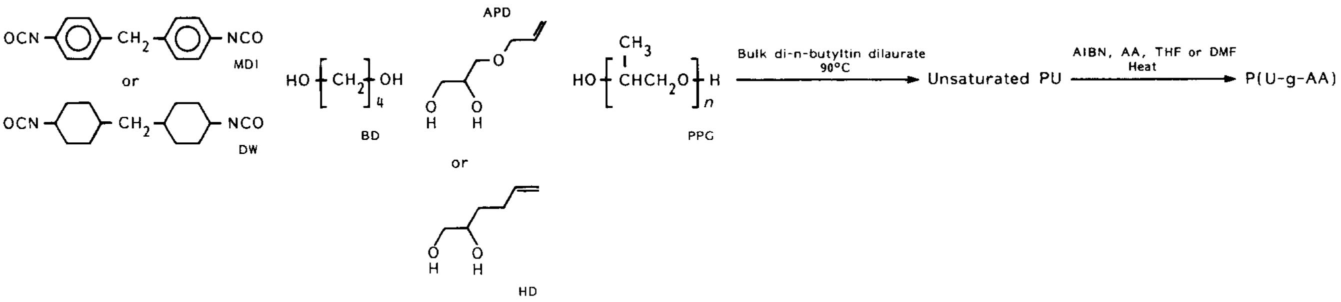

Scheme 1

Bulk polymerization

A number of unsaturated copolymers based on MDI and DW were prepared, with a molar ratio DW or MDI:PPG:BD:HD or APD equal to 10:3:4:3. The BD and unsaturated diol, or PPG and BD, ratios were also varied to give variations in the quantities of double bonds and soft segments incorporated. The methods of synthesis were slightly different due to MDI being much more reactive than DW.

For DW copolymers, DW, PPG, and T12 were heated at 90°C for 0.5 h with occasional stirring. BD and APD (or HD) were added in their appropriate ratios. The viscous homogeneous mixture was vigorously stirred for 5 min. Heating was then resumed for 2 h with occasional turning of the container to effect mixing.

With MDI copolymers, the catalyst was not used. MDI and PPG were heated at 90°C for 1.5 h with stirring. BD and APD (or HD) were then added with stirring. The homogeneous mixture was then heated as before to complete reaction.

Grafting with acrylic acid

Grafting in DMF as solvent will be discussed in the Results section where variations in reagent concentrations will be considered.

The quantities of polyurethane (PU), AA, and AIBN used in THF as solvent are listed in *Table 1* (AA% = (wt of AA/wt of PU) × 100). In general, the polyurethane and AA were dissolved separately in 5 times (wt/vol) THF. The two solutions were combined and 5% (w.r.t. PU mass) AIBN was added. The reaction flask was stoppered. The mixture was then heated and magnetically stirred in a water bath at 60°C for 24 h. The grafted copolymer, P(U-g-AA), was precipitated from distilled water and was immersed in fresh distilled water with continued agitation, for 2 d before drying *in vacuo* at room temperature for 2 weeks.

Titration with NaOH

The AA content in each of the grafted copolymers was determined by titration with sodium hydroxide solution of known concentration.

The grafted copolymer (0.500 g) was dissolved in 20 cm^3 of DMF. Three Pasteur pipette drops of cresol red indicator (0.1% w/v concentration made up in 50:50 water/ethanol mixture) were added to give a yellow coloured solution. It was titrated with 0.5% NaOH in methanol (wt/vol) to the end-point as indicated by a colour change of the solution to purple. A blank with the ungrafted polymer was run and the titration values were corrected accordingly.

Table 1 Reagents used in grafting experiments with THF as solvent

AA%[a]	PU (g)	AA (g)	AIBN (g)	THF (cm^3)
50	40	20	2	300
25	40	10	1	250

[a] Calculated w.r.t. the initial mass of PU

Solvent uptake

Each copolymer (6.00 g) was cast from THF (30 cm^3) onto a 10 cm diameter Petri dish. A regularly shaped film was cut and dried *in vacuo* at room temperature to constant weight. Distilled water was added and the absorption was measured as a function of time by wiping and weighing the film until equilibrium uptake was reached.

The same procedure was repeated, but substituting water with ethanol as solvent.

RESULTS AND DISCUSSION

In DMF

The percentage of acrylic acid grafted onto the unsaturated polyurethane was determined by gel permeation chromatography (g.p.c.) with DMF as eluent, using a PLGel 5μ mixed column at a flow rate of 1 $cm^3 min^{-1}$. The grafted copolymers formed aggregates due to the partial ionization of the acid groups, otherwise known as the polyelectrolyte effect[6]. Two peaks were observed in g.p.c. analysis after the removal of any of the homopolymer polyacrylic acid in the precipitation stage. The lower molecular weight peak was probably due to ungrafted or very slightly grafted polyurethane. The high molecular weight peak, or aggregated peak, could be eliminated by the addition of 0.1% w/v LiBr in the mobile phase. The percentages quoted in this section, designated GPC%, are due to signals of the aggregated peaks analysed with the ultraviolet (u.v.) detector.

A solution containing a mixture of the ungrafted polymer and pure polyacrylic acid analysed with g.p.c. did not show the above mentioned aggregated peaks.

Copolymers based on HD were studied in DMF as solvent.

The percentage grafting was shown to be proportional to the quantity of AIBN used. *Table 2* shows the GPC% values related to the AIBN concentration, with respect to the initial polyurethane weight. The reaction conditions were 73°C, 22 h, with reactants concentration (PU + AA to DMF) of 10% w/v, using a 1:1 ratio of PU to AA. A value of 5–7% initiator concentration was found to be adequate.

Table 2 Dependence of percentage grafting determined by g.p.c. (GPC%) on AIBN%[a]

	PU sample		
	1	2	3
AIBN%[a]	15	7	5
GPC%	96	83	80

[a] Calculated as a percentage of the original PU mass

Table 3 Dependence of percentage grafting determined by g.p.c. (GPC%) on reactants concentration

Sample	1	2	3	4
PU+AA in reaction mixture (%w/v)	20	17	14	12.5
GPC%	Gelled	97	78	70

With the same PU to AA ratio, it was found that a reactants concentration of about 20% led to gelation when using 7% AIBN. The results are shown in *Table 3*. The optimum reactants concentration (PU+AA) is approximately 17% w/v. The free radical sites on a polymer chain or at the end of the polyacrylic branches may combine with similar groups of neighbouring chains when the concentration is too high, and hence gelation results.

Keeping all other conditions constant, the concentration of double bonds was varied. The amount of grafting which resulted varied accordingly, e.g. an initial yield of 81% was reduced to 55% when the number of double bonds in the polymer chain was halved.

The variation of the amount of AA used, and hence the amount of AA subsequently grafted had a direct effect on the physical properties of the copolymer. With a ratio of PU to AA less than 1, the reaction product did not precipitate from water. Micelles or emulsions were formed. Retrieval of the graft was achieved by preferential salting out with sodium chloride and the use of an ultra-centrifuge, or by precipitation from ether. The grafted polymers produced were hard and brittle, and swelled enormously in water.

Table 4 shows the g.p.c. results for products with lower initial AA concentrations, which were precipitated from water. Also included for comparison are values using THF as solvent at 60°C. Grafting was, therefore, feasible at a slightly lowered temperature with little effect upon the graft yield if the reaction time was long enough.

In THF

When THF was employed as solvent, the reaction temperature was reduced to 60°C, with an optimum reactants concentration of 17% w/v and 5% w/w (w.r.t. PU) of AIBN. The reaction time was 24 h. Variations in the concentration of double bonds and AA were considered. Titration results were used to calculate quantitatively the mass of AA present in the polymer. The percentage grafting is defined by the following equation:

$$\%\ \text{grafting} = \frac{\text{mass of AA grafted}}{\text{mass of graft copolymer}} \times 100$$

These values are lower than the GPC% values.

The general trend, as seen from the percentage grafting results in *Table 5*, is that the grafting increases with AA and the number of double bonds available. (DA was a copolymer with a molar ratio DW:PPG:BD:APD equivalent to 10:3:4:3, D(2/3)A = 10:3:5:2, and D(1/3)A = 10:3:6:1 etc.) DW-based copolymers tended to be fractionally more efficient in giving grafted polyurethanes. Probably, the saturated cyclohexane ring exerts a smaller electronegative pull on the neighbouring bonds than the aromatic ring, and being more flexible in its conformation, may open up the double bond branches for more ready free radical addition.

Increasing the soft block content, but keeping the number of double bonds constant appeared to have increased the percentage grafting, although the changes are relatively small, e.g. 9.3, 10.0 and 10.9% grafting when the PPG contents were 3, 4 and 5 parts respectively to 10 parts of DW.

Solvent uptake

The solvents investigated were water and ethanol. The equilibrium percentage solvent content was calculated from the following equation:

$$\text{Equilibrium \% solvent content} = \frac{\text{weight of solvent absorbed}}{\text{initial weight of film}} \times 100$$

In water, the time required to reach equilibrium uptake was approximately 400 h. The films became opaque as the water content increased. As seen in *Table 6*, equilibrium water content increases with increased acrylic acid content in the graft polyurethane. MDI-based polyurethanes appeared to be more hydrophilic than those based on DW. However, the differences were small and not very significant.

The time required to achieve equilibrium in ethanol was much shorter, usually approximately 100 h. Swelling was most marked in DW-based copolymers, although the films remained relatively transparent. MDI-based copolymers, again, became opaque. The films were generally much weaker than those in water. Some, especially those based on MDI, started to disintegrate mechanically. After being immersed in water, it was noted that MDI-based films having a higher APD content in the polymer chain were most prone to crack. HD-based graft copolymers were less inclined to disintegrate mechanically. The electronegative oxygen of the APD branch may lead to weaker cohesion of the hard block domains in the polyurethanes.

With the corresponding DW-based films, however, the reverse behaviour was observed. DH50 (a DW-based P(U-g-AA) with HD as short chain diol and 50% w/w AA initial concentration w.r.t. PU) and DH25 disintegrated mechanically within hours of immersion in ethanol

Table 4 Dependence of grafting determined by g.p.c. (GPC%) on the initial AA concentration

	DMF		THF	
Sample	1	2	1	2
AA%[a]	75	50	50	25
GPC%	94	81	82	75

[a] Calculated w.r.t. the initial mass of PU

Table 5 Percentage grafting by titration with NaOH

AA%[a]	DA[b]	D(2/3)A[c]	D(1/3)A[d]	MA[b]	M(2/3)A[c]	M(1/3)A[d]	DH[b]	D(2/3)H[c]	D(1/3)H[d]	MH[b]	M(2/3)H[c]	M(1/3)H[d]
50	16.8	16.4	8.2	18.8	12.9	11.2	18.0	16.9	10.9	13.0	11.3	14.8
25	9.3	10.1	8.0	11.0	7.1	3.3	11.5	8.9	7.2	9.5	8.7	6.2

D = DW, M = MDI, A = APD, H = HD

[a] Calculated w.r.t. the initial mass of PU

[b] XY denotes a PU of molar ratio X:PPG:BD:Y equal to 10:3:4:3

[c] X(2/3)Y denotes a PU of molar ratio X:PPG:BD:Y equal to 10:3:5:2

[d] X(1/3)Y denotes a PU of molar ratio X:PPG:BD:Y equal to 10:3:6:1

Table 6 Equilibrium percentage solvent contents

	DA50[a]	DA25[b]	MA50[b]	MA25[b]	DH50[a]	DH25[b]	MH50[a]	MH25[b]	MA[c]	D(1/3)A[d]
Water	34.8	13.7	36.1	15.6	31.5	13.3	32.4	16.1	4.4	2.9
Ethanol	300	260	90	50	–	–	76	61	34	95
Selectivity ratio	8.6	19.0	2.5	3.2	–	–	2.3	3.8	7.7	32.8

D = DW, M = MDI, A = APD, H = HD

[a] XY50 denotes a P(U-g-AA) based on the diisocyanate X and the unsaturated diol Y, with an initial AA reactant concentration of 50% w.r.t. the initial PU mass

[b] XY25 denotes a P(U-g-AA) based on the diisocyanate X and the unsaturated diol Y, with an initial AA reactant concentration of 25% w.r.t. the initial PU mass

[c] XY denotes a PU based on the diisocyanate X and the unsaturated diol Y

[d] X(1/3)Y denotes a PU of molar ratio X:PPG:BD:Y equal to 10:3:6:1

and became too weak to handle. The higher the acrylic acid content, the lower was the mechanical strength of the film when saturated with ethanol. DW-based grafted polyurethanes absorbed 3–5 times more ethanol than MDI-based ones. This was due to the fact that the former was more compatible with the organic solvent.

Two ungrafted copolymers MA and D(1/3)A have been included for comparison. The results show that grafting with acrylic acid increases the solvent absorption of the polyurethanes. Equilibrium ethanol uptake is much higher than water. The selectivity ratios, defined as the ratios of ethanol uptake to water uptake, are also given in *Table 6*. These may be related to changes in the domain structures as the amounts of acrylic acid incorporated into the polyurethanes were varied.

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