The γ-radiation induced grafting of unsaturated segmented polyurethanes with *N*-vinyl pyrrolidone

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(*Received 29 September 1983; revised 23 November 1983*)

Linear unsaturated segmented polyurethanes have been modified by hydrophilic grafting at 40°C with *N*-vinyl pyrrolidone, in *N,N*-dimethylformamide as solvent, using ^{60}cobalt γ-irradiation. Graft copolymers were isolated from homopolymers by selective solvent extraction using a Soxhlet apparatus. The effects of reaction time, total dose, temperature and monomer concentration, on the graft yields have been examined. Relatively high irradiation doses were avoided during the grafting experiments to prevent possible degradation of the segmented polyurethanes and gelation of the homopolymer, poly(*N*-vinyl pyrrolidone). The ungrafted and grafted copolymers were characterized, and the graft copolymers were shown to be more thermally stable than the original polyurethanes, by thermogravimetric analysis. An explanation for the observed variation of the graft yields with some of the experimental variables is suggested.

(Keywords: grafting; polyurethane; *N*-vinyl pyrrolidone; γ-radiation; unsaturated polyurethane; segmented polyurethane)

INTRODUCTION

High energy irradiation provides a powerful technique for the radical synthesis and modification of polymeric materials. Thus, radiation-initiated processes have attracted considerable interest in the research, development and technology of various polymers[1-5]. Segmented polyurethanes prepared from poly(tetramethylene glycol) have good mechanical properties and are relatively hydrophobic. However, a variety of biomedical drawbacks are associated with the hydrophobic character of the surfaces of such polyurethanes, including the adsorption of cellular elements in the blood[6-10].

However, hydrophilic, polymeric crosslinked gels, (hydrogels) are generally known to be blood compatible prosthetic materials and have shown promise for cardiovascular applications[11-14]. Nevertheless, they possess relatively poor mechanical properties.

Therefore, grafting of hydrophilic monomers onto segmented polyurethanes offers an attractive technique for improving the properties of these materials by maintaining simultaneously some of the properties of the backbone polymer and the side chain graft polymer. The resulting graft copolymers may therefore possess interesting characteristics in comparison to normal polyblends.

As part of a continuing programme in our laboratories to improve the properties of synthetic polymers and evaluate the possible use of the resulting materials as biomaterials in hemodialysis, we report in this paper the ^{60}cobalt gamma irradiation grafting of *N*-vinyl pyrrolidone onto segmented polyurethanes. The influence of reaction time, total dose, temperature and monomer concentration on the graft yield was investigated. There was good agreement between the theoretically predicted graft yields and the experimental values in the gamma irradiation and AIBN grafting methods.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol), (Quaker Oats Co.), was purified by drying in a vacuum oven at 120°C for 5 h to remove traces of moisture present.

Methylene bis(4-phenyl isocyanate), MDI, (Bayer Ltd., as Desmodur 44MS), was purified by fractional distillation using a jacketed Vigreux column under nitrogen at reduced pressure, immediately before use, to give a white crystalline solid, (m.p. 38°C).

Cis-2-butene-1,4-diol, (Aldrich Chemicals Co. Ltd.), was dried with a Linde molecular sieve, type 5A, for 48 h and fractionally distilled under a reduced pressure of nitrogen.

N-vinyl pyrrolidone, (Aldrich Chemicals Co. Ltd.), was purified by stirring over Linde molecular sieve, type 5A, and then fractionally distilled under reduced nitrogen pressure.

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

4-Methyl pentan-2-one, (Aldrich Chemical Co. Ltd.), was purified by stirring over calcium hydride for 48 h before fractional distillation under nitrogen.

Dimethyl sulphoxide, DMSO, (Hopkin and Williams), was purified by first drying with Linde molecular sieve, type 5A, for 24 h and then stirring over barium oxide for a further 24 h. The dried DMSO was fractionally distilled under nitrogen at reduced pressure.

N,N-dimethylformamide, DMF, (BDH Chemicals),

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was purified by drying over Linde molecular sieve, type 5A, and fractionally distilled from barium oxide under nitrogen at reduced pressure.

Preparation of unsaturated segmented polyurethane copolymers

Relatively high molecular weight segmented polyurethane copolymers, PTM and PUG were synthesized from the reactants shown below according to the method described by Lyman[15] and in our previous papers[16-17]. The overall molar concentrations of the hydroxyl and isocyanate groups were equal in these preparations.

(i) Polyurethane (PTM), was based on methylene bis(4-phenyl isocyanate) (31.53 g), poly(tetramethylene glycol) (10.00 g), *cis*-2-butene-1,4-diol (6.16 g) and butane-1,4-diol (4.14 g), and

(ii) Polyurethane (PUG) was based on poly(ethylene glycol) (21.43 g), Methylene bis (4-phenyl isocyanate) (17.78 g), butane-1,4-diol (2.57 g) and *cis*-2-butene-1,4-diol (2.51 g).

The number average molecular weights of polyurethanes, PTM and PUG, (determined by gel permeation chromatography (g.p.c.)), were 35000 and 30000, respectively. After characterization, the polymers were modified by subsequent grafting experiments.

Synthesis of graft copolymers

Weighed samples of an unsaturated polyurethane copolymer (PTM) and *N*-vinyl pyrrolidone were dissolved in *N,N*-dimethylformamide (DMF) and placed in glass ampoules. After degassing the contents of the ampoules four times, the ampoules were sealed off under vacuum. Irradiation was performed at 40°C using a ^{60}cobalt gamma source with a dose rate of 1.0 Mrad h^{-1}. After the graft copolymerization reactions, the products, (grafted polyurethane, ungrafted polyurethane and poly(*N*-vinyl pyrrolidone)), were precipitated in water. The graft copolymer was then isolated by selective solvent extraction of the polymer mixture with water to remove the poly(*N*-vinyl pyrrolidone), and later with tetrahydrofuran to remove ungrafted polyurethane in a Soxhlet apparatus, as described elsewhere[16]. The extraction procedure was continued until a constant mass of the dried graft copolymer was obtained.

Graft copolymerization reactions of *N*-vinyl pyrrolidone with polyurethane (PTM) were carried out using identical grafting procedures but with varying reaction times, total doses, temperatures and monomer concentrations.

RESULTS AND DISCUSSION

Radiation-induced reactions in polymeric materials are initiated by the formation of excited molecules, ions and free radicals. Some polymers predominantly crosslink when irradiated, whereas others may degrade. In the presence of monomer, the free radicals so produced may initiate chain reactions leading to the formation of graft copolymers and homopolymer.

Using the ^{60}cobalt irradiation technique, various graft copolymers reported in this study were prepared in a homogeneous medium (DMF). The radicals initially produced may add to the double bond on the segmented polyurethane backbone and/or to that in the *N*-vinyl pyrrolidone, and may also participate in hydrogen abstraction reactions from the polymer backbone. The various resulting polymer macroradicals can initiate graft copolymerization addition reactions. The *N*-vinyl pyrrolidone monomer may also be involved in radical reactions which eventually form the homopolymer, poly(*N*-vinyl pyrrolidone).

Grafting of *N*-vinyl pyrrolidone onto the unsaturated segmented polyurethanes was confirmed by the increase in mass of the graft copolymers after the removal of the homopolymer, poly(*N*-vinyl pyrrolidone), and also by microanalysis, infra-red and n.m.r. spectroscopy. Similar techniques have been described elsewhere[16] which establish their validity.

The percentage of grafting was calculated as follows:

$$\% \text{ Grafting} = \left(\frac{M_f - M_o}{M_o}\right) \times 100 \qquad (1)$$

where M_o and M_f represent the masses of the original and isolated grafted polyurethane copolymers, respectively. The % ungrafted polyurethane was small, $<10\%$ in most experiments.

The dependence of the percentage grafting on the reaction conditions such as time, dose, temperature and monomer concentration was examined.

Variation of % grafting with time produced by γ-irradiation at 40°C using polyurethane PTM

A series of experiments was carried out at 40°C using constant initial concentrations of *N*-vinylpyrrolidone and the unsaturated segmented polyurethane, PTM, in DMF solution, subjected to γ-irradiation, for different reaction times, t. For a constant dose rate of 1.0 Mrad h^{-1}, the variation of the % grafting at time t, G_t, with reaction time is shown in *Figure 1*. The results indicate that increasing the reaction time in a series of experiments produces an increase in % grafting which approaches a limiting value for long reaction times, G_∞.

Relatively high irradiation doses, although they might have produced a greater value of % grafting, were avoided in these grafting experiments in order to prevent possible degradation or crosslinking of the unsaturated segmented polyurethane copolymers and gelation of the homopolymer, PVP. For example, Jansen *et al.*[3] obtained high graft yields (up to 2000%) in the grafting of hydroxyethylmethacrylate (HEMA) onto a segmented polyurethane using ^{60}cobalt γ-radiation, but gelation of HEMA occurred at high doses. This made the subsequent isolation of the graft copolymers very difficult.

The total rate of disappearance of monomer in any grafting experiment, initiated by γ-irradiation in this case, or by added initiator such as AIBN, R_p, may be expressed in the simplest case by

$$R_p = \frac{-d[M]}{dt} = \frac{k_p[M]I^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}} \qquad (2)$$

where k_p and k_t are velocity constants for propagation and termination (combination and disproportionation), respectively, $[M]$ is the monomer concentration at time t, and I is the rate of initiation.

Integration of (2) at constant rate of initiation, such as constant γ dose-rate in the present experiments, gives

$$\ln([M]_o/[M]) = kt \qquad (3)$$

where $[M]_o$ is the initial monomer concentration and

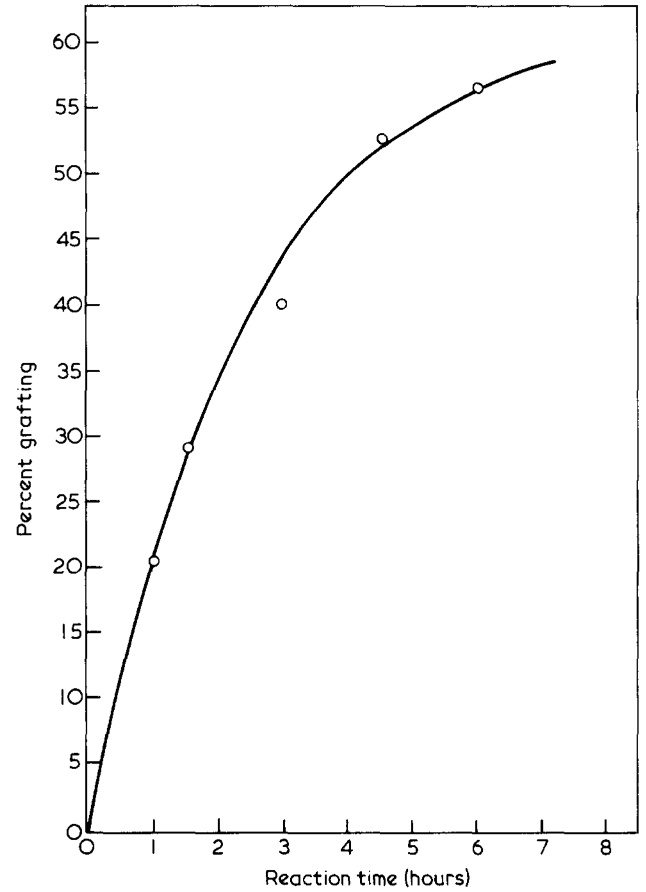

Figure 1 Effect of reaction time, t, on the % grafting, G_t, induced by γ-irradiation. Temperature=40°C; [*N*-vinylpyrrolidone]=0.706 mol dm^{-3}; dose rate=1.0 Mrad h^{-1}; polyurethane, (PTM), 1.00 g; DMF, 25 cm^3

[M] is the concentration at time t, and where

$$k=(k_p I^{\frac{1}{2}}/(2k_t)^{\frac{1}{2}}) \qquad (4)$$

The monomer concentrations are related to the % grafting values if depletion of monomer with increasing time limits the extent of grafting, rather than depletion of double bonds in the polyurethane:

$$\frac{[\mathrm{M}]_0}{[\mathrm{M}]}=\left\{\frac{G_\infty}{G_\infty - G_t}\right\} \qquad (5)$$

which does not imply, however, that all of the monomer is used in the formation of grafts, since some is used in the formation of homopolymer, poly(*N*-vinylpyrrolidone).

From equations (3) and (5), at constant initiation rates,

$$\ln(G_\infty - G_t)=k'-kt \qquad (6)$$

where k' is equal to $\ln(G_\infty)$.

Figure 2A shows a plot of $\ln(G_\infty\ G_t)$ against reaction time t for the ^{60} cobalt irradiation experiments with the polyurethane PTM using a G_∞ value of 60.0. From the slope of *Figure 2A*, the value of k is (0.50 ± 0.04) h^{-1} at 40°C.

Variation of % grafting with initial monomer concentration, at constant reaction time, produced by γ-irradiation at 40°C using polyurethane PTM

A plot of % grafting against initial (*N*-vinyl pyrrolidone) for a constant reaction time of 4.5 h at a dose rate of 1.0 Mrad h^{-1} is shown in *Figure 3*. The marked increase in the % grafting with increase in $[M]_0$ is expected since the molecular weights of the grafts also increase with $[M]_0$. A similar type of behaviour has been noticed previously[16] for grafting produced using AIBN at 80°C with an unsaturated polyurethane based on poly(ethylene glycol).

Variation of % grafting with time produced by initiation with AIBN using polyurethane PUG at 80°C

In a previous study[16], *N*-vinyl pyrrolidone was grafted onto an unsaturated segmented polyurethane based on poly(ethylene glycol), using AIBN as initiator in DMF as solvent, at 80°C. The variation of G_t with t for this series of experiments, using AIBN, gave a plot of similar shape to *Figure 1*, and gave an extrapolated value of G_∞ for infinite time, equal to 35.0.

The plot of $\ln(G_\infty - G_t)$ against time t, using this extrapolated value of G_∞, for this series of experiments is linear, as shown in *Figure 2B*. The radical concentration is again effectively constant in these experiments, and the corresponding value of k in equation (6) is (0.58 ± 0.04) h^{-1}.

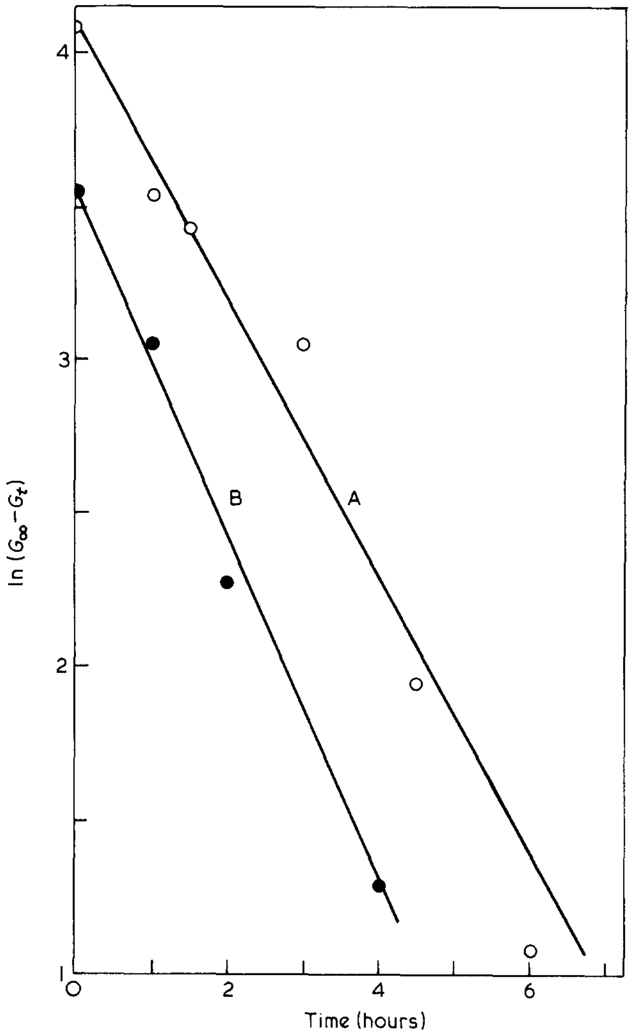

Figure 2 $\ln(G_\infty - G_t)$ as a function of reaction time, t. (A) for γ-irradiation experiments: Temperature=40°C; [*N*-vinylpyrrolidone]=0.706 mol dm^{-3}; dose rate=1.0 Mrad h^{-1}; polyurethane, (PTM), 1.00 g; DMF, 25 cm^3. (B) for grafting induced by AIBN: Temperature=80°C; $[\mathrm{AIBN}]_0=2.4\times10^{-2}$ mol dm^{-3}; [*N*-vinyl-pyrrolidone]$_0$=0.706 mol dm^{-3}; polyurethane, PUG, 1.0 g; DMF, 30 cm^3

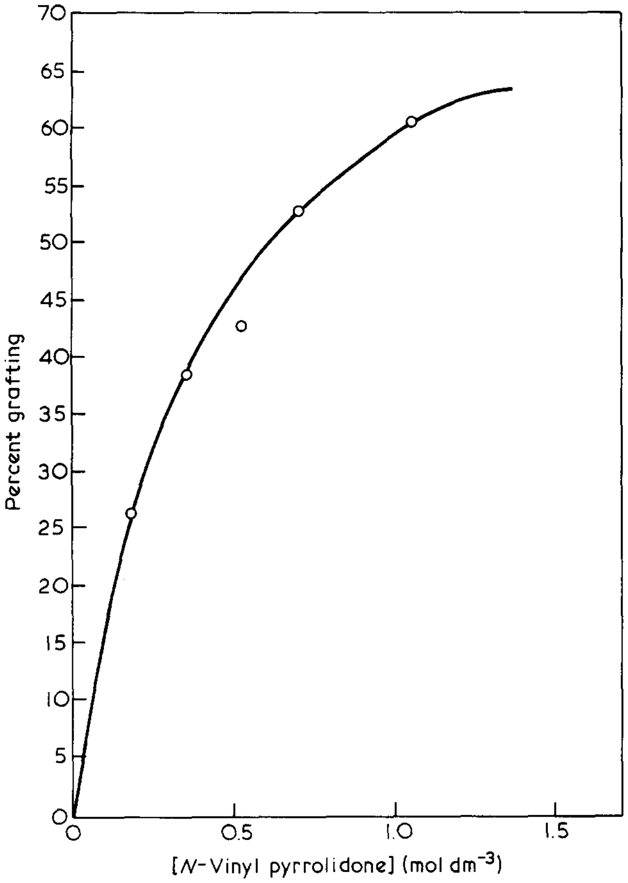

Figure 3 Effect of initial monomer concentration on the % grafting, G_t, induced by γ-irradiation. Temperature=40°C; polyurethane, (PTM), 1.00 g; DMF, 25 cm^3; total γ-dose=4.5 Mrad (constant reaction time of 4.5 h at a dose rate of 1.0 Mrad h^{-1})

Variation of % grafting with initiator concentration for initiation with AIBN using polyurethane PUG at 80°C

In a previous study[16], the % grafting for fixed times of reaction were investigated for an unsaturated polyurethane based on poly(ethylene oxide), PUG, as a function of AIBN concentrations, at 80°C.

A limiting value of % grafting equal to about 44 was approached[16] at high [AIBN]. Theoretically the same limiting values, G_∞, would be predicted both for high times of reaction and for high rates of initiation using AIBN as initiator. Thus from equations (3), (4) and (5)

$$G_t = G_\infty\left\{1-\exp\left(\frac{-k_p I^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}}t\right)\right\} \tag{7}$$

and $G_t \rightarrow G_\infty$ at $t \rightarrow \infty$ and as I (or [AIBN])$\rightarrow\infty$. The observed difference between the value of G_∞ observed in this study at high reaction times and high [AIBN] may be attributed to differences in the kinetic processes producing grafting as the initiator concentration is changed. In particular, kinetic processes involving initiation will change most markedly at high [AIBN].

ACKNOWLEDGEMENTS

The authors wish to thank the A.C.U. for financial support to S.H.E.

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