Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Grafting Vinyl Monomers onto Unsaturated Segmented Polyurethanes. 1. Graft Copolymerization of Acrylamide, Methacrylonitrile, and Methyl Methacrylate

S. H. O. Egboh[a]
[a] Department of Chemistry, Imperial College of Science and Technology, London, United Kingdom

To cite this Article Egboh, S. H. O.(1983) 'Grafting Vinyl Monomers onto Unsaturated Segmented Polyurethanes. 1. Graft Copolymerization of Acrylamide, Methacrylonitrile, and Methyl Methacrylate', Journal of Macromolecular Science, Part A, 19: 7, 1041 — 1048

To link to this Article: DOI: 10.1080/00222338308081083

URL: http://dx.doi.org/10.1080/00222338308081083

J. MACROMOL. SCI.–CHEM., A19(7), pp. 1041-1048 (1983)

Grafting Vinyl Monomers onto Unsaturated Segmented Polyurethanes. I. Graft Copolymerization of Acrylamide, Methacrylonitrile, and Methyl Methacrylate

S. H. O. EGBOH

Department of Chemistry
Imperial College of Science and Technology
South Kensington, London SW7 2AY, United Kingdom

ABSTRACT

Some relatively high molecular-weight unsaturated segmented polyurethanes based on methylene bis(4-phenyl isocyanate), butane-1,4-diol, cis-2-butene-1,4-diol, and poly(propylene glycol) were synthesized and characterized. These unsaturated segmented polyurethanes were chemically modified by grafting acrylamide, methyl methacrylate, and methacrylonitrile in DMF solution using 2,2-azobisisobutyronitrile and benzoyl peroxide as initiators. Attempted graft copolymerizations with other monomers including styrene and sodium styrene sulfonate were unsuccessful. The graft copolymers were isolated by selective solvent extraction in a Soxhlet apparatus. Comparison was made of the efficiency of the initiators and the nature of the monomers on the graft yields. The graft yield was greatly enhanced by increasing the monomer concentration and the reaction time. Some properties of the graft copolymers were studied.

0022-233X/83/1907-1041$3.50/0

INTRODUCTION

The synthesis and characterization of segmented polyurethanes have been extensively studied. The properties of these polyurethanes could be enhanced by chemical modification and thus diversify their different range of utilization. Graft copolymerization of a variety of vinyl monomers onto polyurethane backbones by various methods has been widely reported and represents a technique for the modification of these polymers [1-7].

There have been several references in the literature with regard to the synthesis of graft polyurethanes using acrylamide [8-10]. However, as far as we are aware, these graft copolymers have been prepared using either polyurethane films or foams and therefore grafting occurred on the polyurethane surface.

To our knowledge, no poly(urethane-g-acrylamide)s from unsaturated segmented polyurethanes in DMF solution have been reported previously in the literature. Moreso, due to wide differences in the solubility of polyurethanes and polyacrylamide, it may be useful to study the effect of this solubility on the graft yield. Furthermore, the grafting of acrylamide and other monomers including methacrylonitrile and methyl methacrylate may affect the physical, biological, and chemical properties of these polymers. It is necessary to consider the effects of the free radical initiators and monomers on the graft yields.

This paper reports the synthesis and characterization of unsaturated segmented polyurethanes modified by grafting acrylamide, methyl methacrylate, and methacrylonitrile using AIBN and benzoyl peroxide.

EXPERIMENTAL

Chemicals

Methylene bis(4-phenyl isocyanate), MDI (Bayer U.K. Ltd as "Desmodur 44 MS"), poly(propylene glycol), (BDH Chemicals), cis-2-butene-1,4-diol (Aldrich Chemicals Co. Ltd), and butane-1,4-diol (BDH Chemicals) were purified as described in our previous paper [11]. Acrylamide (BDH Chemicals) was purified by recrystallization from chloroform and then dried in a vacuum oven at room temperature before use.

Methyl methacrylate (BDH Chemicals) contains inhibitors such as hydroquinone. It was purified by washing with 5% sodium hydroxide and dried over anhydrous calcium chloride. The dried MMA was fractionally distilled under reduced pressure. Methacrylonitrile (Aldrich Chemicals Co. Ltd), stabilized with hydroquinone monoethyl ester was purified before use.

Other monomers, such as styrene and sodium styrene sulfonate, were also purified by standard techniques. 2,2-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were recrystallized from ethanol and chloroform, respectively. All solvents used in the synthesis of the unmodified and graft polyurethane copolymers such as dimethyl sulfoxide, 4-methylpentan-2-one, and N,N-dimethylformamide were purified before use [11].

Synthesis of Linear Unsaturated Segmented Polyurethane Copolymers

Two relatively high molecular-weight linear unsaturated segmented polyurethanes designated PU3 and PU4 were prepared from methylene bis(4-phenyl isocyanate), poly(propylene glycol), cis-2-butene-1,4-diol, and butane-1,4-diol by the method described previously [11]. These polyurethanes were further purified by subjecting them to a Soxhlet extraction apparatus using acetone. GPC results showed that the number-average molecular weights of PU3 and PU4 were 32,000 and 35,000 respectively. After characterization of these polymers, they were used for grafting experiments.

Graft Polymerization Procedure

Known weights of polyurethane, monomer, and initiator were dissolved in N,N-dimethylformamide (DMF) in a glass ampule. The ampule was degassed several times by the freeze-thaw cycle method. The ampule was sealed off and thermostated immediately for the polymerization reaction. After the required reaction time, the contents of the ampule were poured into excess water to precipitate the polymers. The resulting precipitate was filtered off and dried in a vacuum oven at 50°C.

The isolation of the graft copolymer was carried out by a similar method as described and shown to be effective, elsewhere [1]. The previously precipitated polymer mixture was subjected to a Soxhlet extraction procedure. Due to the differences in solubility of the homopolymers polyacrylamide, polymethacrylonitrile, and poly(methyl methacrylate), water, acetone, and benzene were used, respectively, as solvents in the Soxhlet extraction until no more extractable homopolymer remained. Gravimetric and GPC analysis showed that all homopolymers were completely removed. The remaining graft copolymers were dried in a vacuum oven at 50°C.

RESULTS AND DISCUSSION

The segmented polyurethanes contain aliphatic double bonds and, as in our previous paper [1], the reduced intensity of the infrared absorption peak due to unsaturation in the graft copolymers suggests that grafting occurs from the aliphatic double bonds. GPC analysis, IR, NMR, gravimetric, and microanalysis results of the graft copolymers differ from those of the ungrafted polymers. The increase in mass of any graft copolymer was due to the added mass of the poly(vinyl monomer) grafts since the homopolymer had been removed.

The percentage of grafting was determined from the difference in the weight of the dried graft copolymers and the dried polyurethanes, defined by

$$\%\ \text{Grafting (w/w)} = \left[\frac{\text{weight of graft copolymer - weight of original polyurethane}}{\text{weight of original polyurethane}}\right] \times 100$$

The effect of reaction conditions on the percentage grafting of acrylamide onto polyurethane (PU3) is shown in Table 1. The grafting of acrylamide with benzoyl peroxide produced graft copolymers with % grafting between 1.3 and 5.7, irrespective of reaction conditions studied. Relatively low graft yields were obtained in the graft copolymerization using acrylamide. The polymerization reactions, though initially homogeneous, became heterogeneous as the reaction progressed due to the insolubilization of both the polyacrylamide and the poly(urethane-g-acrylamide)s. The heterogeneity of the reaction may be responsible for the low graft yields compared to the relatively higher graft yields during the synthesis of poly(urethane-g-N-vinyl pyrrolidone)s [1] although both monomers have different reactivity parameters. The precipitation of the homopolymer (polyacrylamide) and the graft copolymers could further enhance the termination reactions. This heterogeneity in the grafting of acrylamide onto segmented polyurethanes in solution may account for many authors [8-10] effecting grafting of this monomer on polyurethane surfaces by using either the films or foams.

The solubility tests of the graft copolymers showed that they were insoluble in most common organic solvents such as DMSO, THF, DMF, morpholine, dioxane, and also in water. This indicates that the polyurethane backbone is prevented from being solubilized by the polyacrylamide branches. Polyacrylamide is insoluble in most organic solvents and its solubility is limited to water and morpholine. Intramolecular imidization of the polyacrylamide branches is possible but unlikely in these experiments due to the short reaction times. Infrared spectrum of the poly(urethane-g-acrylamide) obtained using a KBr disk showed the absorption bands at 1667 and 3330 cm^{-1} which are characteristic of the $-\text{C}=\text{O}$ stretching vibration and the primary amide group, respectively, of the polyacrylamide branches.

The values of the percentage grafting for the graft copolymerization of methacrylonitrile and methyl methacrylate are shown in Table 2. The nature of the monomer to be grafted onto a polyurethane is known

TABLE 1. Effect of Reaction Conditions on the % Grafting of Acrylamide[a]

Code no.	Time (h)	[AIBN] (mol/dm^3)	Monomer concentration (mol/dm^3)	% Grafting
A1	1.5	3.0×10^{-3}	24.5×10^{-2}	5.24
A2	2.0	3.0×10^{-3}	24.5×10^{-2}	7.88
A3	4.0	3.0×10^{-3}	24.5×10^{-2}	15.49
B1	4.0	5.5×10^{-3}	24.5×10^{-2}	17.20
B2	4.0	1.0×10^{-2}	24.5×10^{-2}	18.41
C1	4.0	1.0×10^{-2}	54.0×10^{-2}	20.13
C2	4.0	1.0×10^{-2}	80.0×10^{-2}	23.07

[a] Polyurethane (PU3) = 1.0 g, 60°C, DMF = 40 cm^3.

TABLE 2. Effect of Reaction Conditions on the % Grafting of Methacrylonitrile (MAN) and Methyl Methacrylate (MMA)[a]

	Initiator		Monomer concentration		
Code no.	[AIBN] (mol/dm^3)	[BPO] (mol/dm^3)	[MMA] (mol/dm^3)	[MAN] (mol/dm^3)	% Grafting
D1	-	5.5×10^{-3}	24.5×10^{-2}	-	6.12
D2	-	1.0×10^{-2}	24.5×10^{-2}	-	7.45
D3	5.5×10^{-3}	-	24.5×10^{-2}	-	0.72
D4	1.0×10^{-2}	-	24.5×10^{-2}	-	0.90
E1	-	5.5×10^{-3}	-	24.5×10^{-2}	3.18
E2	-	1.0×10^{-2}	-	24.5×10^{-2}	7.22
E3	5.5×10^{-3}	-	-	24.5×10^{-2}	0.37
E4	1.0×10^{-2}	-	-	24.5×10^{-2}	0.84

[a] Polyurethane (PU4) = 1.0 g, 60°C, DMF = 40 cm^3, time = 4 h.

TABLE 3. Monomers Used in Graft Copolymerization of Segmented Polyurethanes at 60° C

Monomers	Results
Acrylamide	Successful
Methacrylonitrile	Successful
Styrene	Unsuccessful
Methyl methacrylate	Successful
Sodium styrene sulfonate	Unsuccessful

TABLE 4. Glass Transition Temperatures of the Copolymers

Copolymer	T_g (°C)
Unmodified polyurethane	-37, 160
Poly(urethane-g-acrylamide)	-37, 145
Poly(urethane-g-methacrylonitrile)	-36, 140
Poly[urethane-g-methyl methacrylate]	-38, 150

to affect the graft yields due to its relative reactivity ratio in a copolymerization system. Furthermore, initiator radical or polymer macroradical could also be unreactive toward a particular monomer and hence result in low graft yield. As expected, the graft yields are enhanced by increasing the monomer concentration and reaction time. Attempts were made to graft other vinyl monomers onto the segmented polyurethanes, and the results of these experiments are summarized in Table 3.

The efficiency of any initiator on the graft yields depends on the monomer to be grafted, its concentration, nature of the solvent, temperature, and monomer concentration. AIBN produced relatively higher graft yields than benzoyl peroxide in the grafting of acrylamide. However, grafting of methyl methacrylate and methacrylonitrile with benzoyl peroxide produced higher graft yields than with AIBN. Several authors [12, 13] have reported the influence of initiators such as AIBN and benzoyl peroxide on the grafting of styrene and methyl methacrylate on polymers such as polybutadiene and natural rubber. For example, they attributed the ineffectiveness of AIBN to the resonance stabilization of the 2-cyano-2-propyl radicals produced from the initiator.

The results of differential thermal analysis are shown in Table 4.

The differential thermal analysis of the polymers (DSC) did not show the glass transition temperatures for the grafted vinyl monomers. The thermograms of the graft copolymers showed two distinct transition temperatures at about -37°C due to the T_g of the soft segment and a shifted peak (reduced) around 145°C due to the melting of the hard segment polyurethane blocks. Microphase separation giving rise to a different phase for the grafted branches is not anticipated because the average degree of polymerization of the poly(vinyl monomer) grafts is low. Therefore, the added grafts seem to act as diluents for the hard segment block.

Thermogravimetric analysis of the polyurethanes was performed in a dry nitrogen atmosphere. The results indicate that graft copolymerization of acrylamide and methacrylonitrile enhances the thermal stability of polyurethane while poly(urethane-g-methyl methacrylate)s have lower thermal stability than the original polyurethanes. Therefore, it seems that the thermal stability of graft polyurethane copolymers depends on the type of monomer grafted and the extent of grafting. This trend has been observed previously with regard to the thermal stability of other natural and synthetic polymers [2, 14-16]. A difference in the thermal degradation mechanisms of the grafted and ungrafted polyurethanes may be involved.

REFERENCES

[1] H. S. Egboh, M. H. George, J. A. Barrie, and D. J. Walsh, J. Polym. Sci., Polym. Chem. Ed., 20, 2879 (1982).

[2] K. Adibi, M. H. George, and J. A. Barrie, Polymer, 20, 483, (1979); J. Polym. Sci., Polym. Chem. Ed., 19, 57 (1981).

[3] B. Jansen and G. Ellinghorst, J. Polym. Sci., Polym. Symp., 66, 465 (1979).

[4] H. C. Beachell and J. C. Peterson Buck, J. Polym. Sci., Part A-1, 7, 1873 (1969).

[5] W. C. Karyla and R. D. Whitman, J. Appl. Polym. Sci., 11, 133 (1967).

[6] A. S. Koffman and W. G. Kraft, Am. Chem. Soc., Polym. Prepr., 13(2), 723 (1972).

[7] N. Yoshinobu, I. Hiroshi, and W. Takeaki (Matsushita Electric Works Ltd.), Japan Kokai, 75 03,475 (C1.25 (5) J12, 25(9) D121,41), January 14, 1975; Chem. Abstr., 83, 29380Y (1975).

[8] W. J. Skraba and J. W. Lynn, Irradiation in Polymer, Vol. 66 (Advances in Chemistry Series, R. F. Gould, ed.), American Chemical Society, 1967, p. 214.

[9] F. W. Meisel, Jr., and E. A. Blair, Canadian Patent 802,956 (1968).

[10] W. Karo, Research on Non-Thrombogenic Biomaterials, Polysciences, Inc., Warrington, Rhode Island, Epon 812.

[11] S. H. Egboh, A. Ghaffer, M. H. George, J. A. Barrie, and D. J. Walsh, Polymer, 23, 1167 (1982).

[12] H. A. J. Battaerd and G. W. Tregear, Graft Copolymers, Wiley-Interscience, New York, 1970.
[13] R. E. Wetton, J. D. Moore, and B. E. Fox, Makromol. Chem., 132, 135 (1970).
[14] V. N. Sharma and E. H. Daruwalla, J. Appl. Polym. Sci., 21, 331 (1977).
[15] P. L. Nayak, S. Lenka, and N. C. Pati, Angew. Makromol. Chem., 96, 131 (1981).
[16] D. S. Varma and V. Narsimhan, J. Appl. Polym. Sci., 16, 3325 (1972).

Accepted by editor October 5, 1982
Received for publication November 5, 1982