Polymer Networks Containing Degradable Polyacetal Segments

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ABSTRACT: Telechelic poly(1,3-dioxolane)s (polyDXL) with methacrylate end groups have been synthesized by cationic ring-opening polymerization of DXL, carried out in the presence of methylenebis(oxyethyl methacrylate) as an end blocker. If the initiator concentration is negligible compared with the end-blocker concentration, the molecular weight of the thus obtained polyDXL is governed by the ratio of reacted monomer to reacted end blocker. Radical copolymerization of the α,ω-bis(methacrylate)-terminated polyDXL leads to the formation of polymer networks in which the polyDXL acts as a polymeric cross-linking agent. The resulting materials are insoluble in any solvent and swell in good solvents for the corresponding linear polymers. Since the ceiling temperature of the polyDXL is low, the thus obtained networks can be de-cross-linked under mild conditions by treatment with a trace of cationic initiator. In the presence of alcohols, the degradation is retarded and acid-catalyzed hydrolysis of the networks failed completely. However, the thermal stability of the acid-treated networks is markedly lower than that of untreated samples.

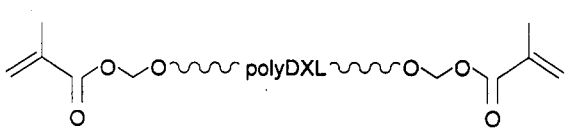
Introduction

The use of macromonomers for the synthesis of graft copolymers is well documented in the last decade. Numerous examples of macromonomer synthesis by different polymerization mechanisms and several studies on their copolymerization behavior have been reported.[1,2] Polymers containing two polymerizable end groups, designated as "telechelic bismacromonomers", have not been described so frequently. Copolymerization of such bismacromonomers is expected to lead to polymer networks in which homopolymeric segments of one monomer are connected by the macromonomer segments. In this way it should be possible, by a combination of selected (co)monomers and macromonomers, to build a whole series of novel networks with well-defined segmental structures.

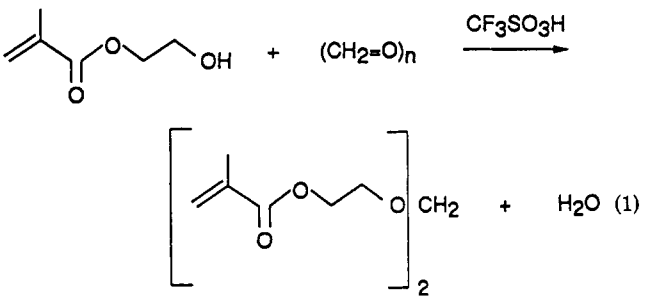
In the present paper we describe the synthesis of segmented networks based on a bismacromonomer of poly(1,3-dioxolane) (polyDXL). Since polyDXL has a low ceiling temperature,[3] the thus obtained networks contain segments which are expected to degrade to monomer under mild conditions by treatment with a trace of an appropriate cationic initiatior. Such networks may be interesting from at least two viewpoints: first, solubilization of cross-linked polymers under mild conditions may be useful in itself, and, second, the possibility to study the soluble residual linear polymer chains may be used to obtain more insight in the copolymerization behavior of monomers and macromonomers under network-forming conditions.

Results and Discussion

1. Synthesis of PolyDXL Bismacromonomer. PolyDXL α,ω-bis(methacrylate ester) has been prepared earlier by end-capping the bifunctionally living polyDXL with triethylamine, followed by nucleophilic substitution of the ammonium groups by a methacrylate anion.[4] The bifunctional living polymer was obtained by polymerization of DXL with terephthaloyl bis(trifluoromethanesulfonate) at −30 °C. In the thus obtained bismacromonomer the methacrylate groups are present as a hemiacetal ester function:



In the present work we used a new synthesis of telechelic polyDXL, i.e., by polymerization of DXL in the presence of dialkylformals as chain-transfer reagents, the so-called end-blocker method.[5] The method is based on the assumption that the intermolecular chain transfer to the acetal functions of the polymer chain—a well-known characteristic of the cationic polymerization of cyclic acetals[6]—will also occur with added functional acetals. This chain-transfer reaction has been used before to control the molecular weight of polyacetals[7-9] but to the best of our knowledge it has not yet been employed to produce telechelic polymers. In the present work we prepared methylenebis(oxyethyl methacrylate) (I), the formal of 2-hydroxyethyl methacrylate (HEMA), by reaction of HEMA with paraformaldehyde in the presence of triflic acid (eq 1).



(1)

Figure 1 shows the ^{1}H NMR spectrum of I. When I is used as an end blocker, polyDXL α,ω-bis(methacrylate) (II) is obtained in a one-step procedure. In this case the methacrylate groups are linked to the polymer chain by an ester function (Scheme I).

The methacrylate ester end groups are clearly visible in the ^{1}H NMR spectrum of II as shown in Figure 2. The average degree of polymerization DP_n of the linear fraction of the polymer is given by

$$DP_n = \frac{m_0 - m_e - m_c}{[I]_0 + [T]_0 - [T]_e}$$

where m_0 and m_e are the initial and equilibrium monomer concentrations and m_c corresponds to the concentration of the monomer which has formed cyclic oligomers. $[I]_0$ is the initiator concentration and $[T]_0$ the initial concentration of the transfer reagent. $[T]_e$ is the equilibrium concentration of the transfer agent. At 20 °C, m_e is

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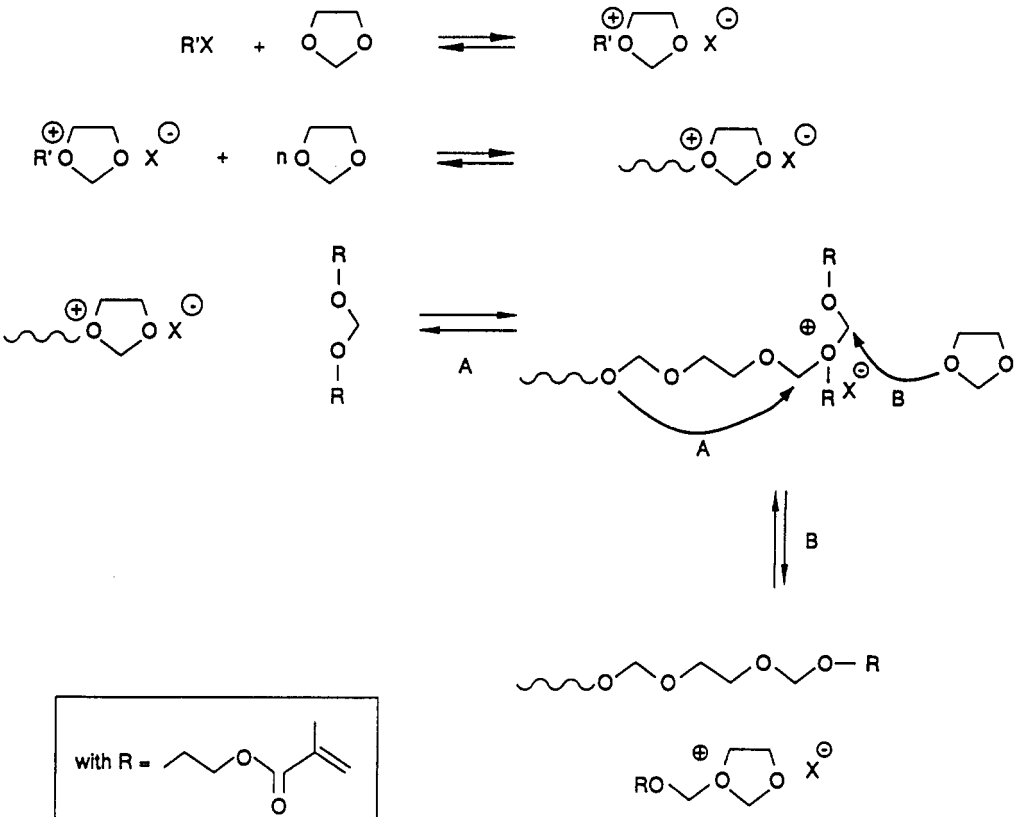
Scheme I



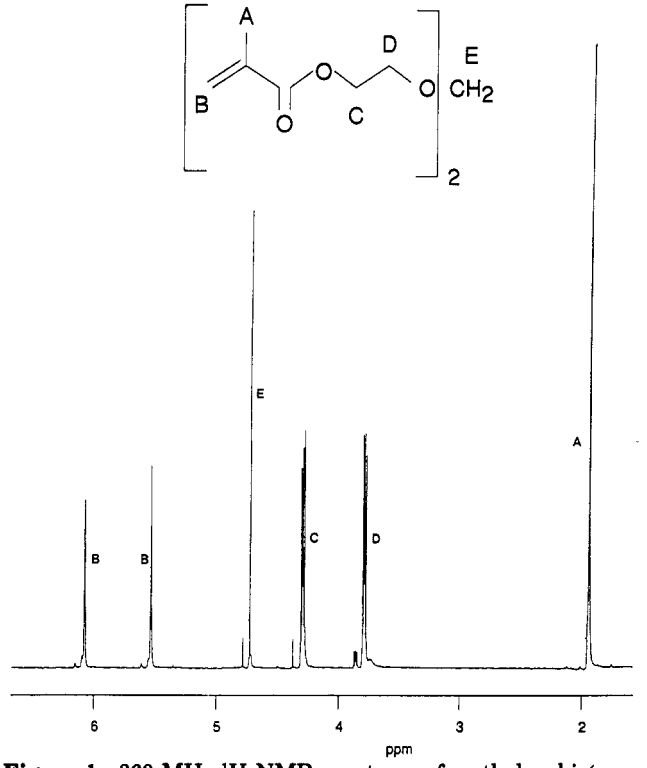


Figure 1. 360-MHz ^{1}H NMR spectrum of methylenebis(oxyethyl methacrylate).

estimated to be 1.0 mol·L^{-1} [3] and m_c 0.8 mol·L^{-1}.[10] If the initiator concentration is low compared with the transfer concentration, the DP_n is expected to be given by

$$DP_n = \frac{(m_0 - 1.8)}{[T]_0 - [T]_e}$$

The value of $[T]_e$ is experimentally determined by GLC

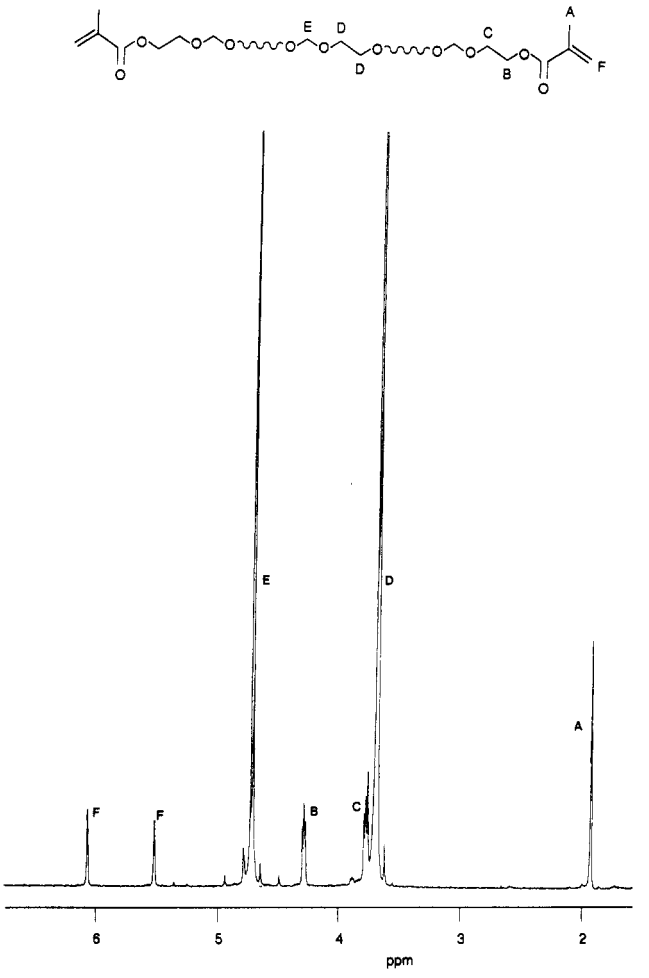


Figure 2. 360-MHz ^{1}H NMR spectrum of α,ω-bis(methacrylate)-terminated polyDXL.

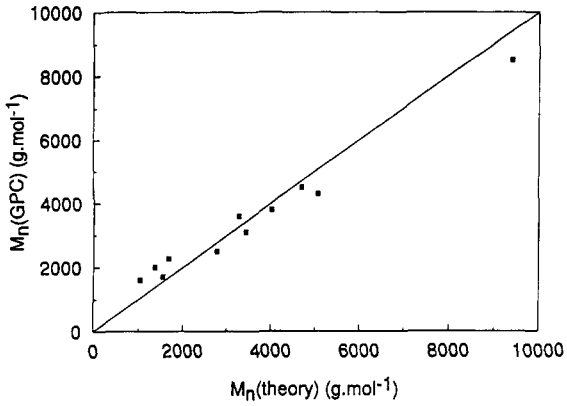


Figure 3. Control of the molecular weight of polyDXL with methylenebis(oxyethyl methacrylate) as end blocker. Polymerization initiated with methyl triflate in CH_2Cl_2 at 20 °C.

at the end of the polymerization. It was found to be directly proportional to $[T]_0$ and inversely proportional to $(m_0 - m_e)$. As shown in Figure 3 the variation of M_n (which equals $74(DP_n) + 272$) as a function of $\Delta m/\Delta[T]$ for polymerizations carried out in the presence of varying amounts of end blocker is in good agreement with the expected values. Analysis of the polymers by ^1H NMR spectroscopy, in combination with their molar masses, determined by GPC, leads to the conclusion that the end-group functionalities of the thus obtained polymers are between 1.8 and 2.0. Table I gives a survey of the experimental conditions used to synthesize II with different molecular weights.

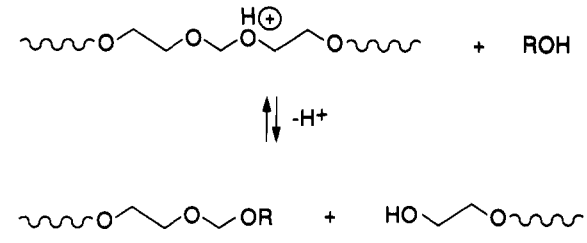
2. Copolymerization of the Bismacromonomers. Three monomers have been selected for the copolymerization studies of II: methyl methacrylate (MMA), butyl acrylate (BA), and styrene (ST). The copolymerizations were conducted in toluene at 70 °C with 2,2′-azobis(2-methylpropionitrile) as initiator. In all cases the reaction mixture gelled after less than 30 min. The polymerizations were continued for 16 h. The end products obtained with MMA and ST were glassy, brittle materials and those obtained with BA were elastomers. A dynamic mechanical thermal analysis (DMTA) of the latter is shown in Figure 4. This analysis shows a number of T_g's in the temperature region corresponding to the T_g's of polyBA (approximately −32 °C) and of polyDXL (approximately −40 °C). The increase of log E' at −20 °C is explained by the occurrence of dynamic crystallization of the polyDXL segments. Also at room temperature a slow crystallization of the polyDXL is observed.

Networks composed of polyDXL and polyMMA (50/50 by weight) show no crystallization of the polyDXL at any temperature. Apparently, the rigid polyMMA chains lower the flexibility of the polyDXL segments and prevent their crystallization. The differences in the crystallinities of poly(BA-*g*-DXL) and poly(MMA-*g*-DXL) networks with a similar composition and the same thermal histories is also shown by DSC analysis (Figure 5): the endotherm at 300 K due to the melting of the polyDXL segments in the DSC of the former is completely absent in that of the latter.

All materials are insoluble in any solvent but swell in good solvents for the corresponding linear polymers. The degrees of swelling of a network obtained with MMA in different solvents are reported in Table II. The fraction of materials extractable with THF, a good solvent for polyDXL, was in all cases lower than 2%.

3. De-Cross-Linking of the Networks. In principle, two methods for chain scission in the above-mentioned

Scheme II



networks can be envisaged. The first is based on the low ceiling temperature of polyDXL and the second on the hydrolytic instability of the acetal function in the presence of an acid.

At room temperature the equilibrium concentration of the DXL monomer is approximately 1 mol·L^{-1} and that of the cyclic oligomers approximately 0.8 mol·L^{-1} (expressed in monomer units). Consequently, if the networks are allowed to swell in a solvent containing an initiator for the degradation, the polyDXL segments are expected to degrade until these equilibrium concentrations are reached, i.e., up to a total monomer unit concentration of approximately 1.8 mol·L^{-1} or about 20% by weight. Considering that the networks may contain 20% or less polyDXL segments, this means that even with small amounts of solvent (containing the initiator), a complete degradation of the polyDXL, and consequently a complete solubilization of the network, should occur.

Table III describes some examples of de-cross-linking experiments, performed with a poly(MMA-*g*-DXL) network under different conditions. From this table it follows that with organic solvents containing a strong acid such as triflic acid, solubilization occurs at room temperature in 20 min. It also follows that the presence of an alcohol retards the degradation reaction. This was surprising since it was expected that an alcohol, in the presence of an acid, would give a trans-acetalization reaction with chain scission (Scheme II). Apparently, the hydroxyl functions, due to their higher basicity, reduce the protonation of the acetal groups and hence the rate of degradation.

Attempts to de-cross-link the networks by acid-catalyzed hydrolysis in aqueous solution failed completely. A network obtained with MMA, containing 50% of polyDXL, remained insoluble for several months in a 1 M aqueous solution of triflic acid. However, the thermal stability of the acid-treated material after removal of the solvent was markedly lower than that of the untreated one. This is demonstrated by comparison of the thermogravimetric analysis of a sample which has been treated with acid with that of an untreated one. As shown in Figure 6, the untreated sample shows two distinct degradation temperatures: one around 250 °C, typical for ester end-capped polyDXL, and a second one around 370 °C, typical for polyMMA. The acid-treated sample shows its first degradation at 85 °C, a shift of 165 °C with respect to the original material.

4. Analysis of the De-Cross-Linked Polymers. After complete degradation of the polyDXL segments, the remaining polymer should have the structure of a random copolymer of HEMA and the other comonomer. Quantitative analysis by ^1H NMR spectroscopy permits us to determine the fraction of HEMA in the copolymer and thus to check what fraction of the originally introduced macromonomeric methacrylate functions has actually participated in the copolymerization reaction. Figure 7 shows the ^1H NMR spectrum of the MMA–HEMA copolymer obtained after the de-cross-linking of a network formed by copolymerization of II with M_n = 3600 and in

Table I
Polymerizations of DXL in the Presence of Methylenebis(oxyethyl methacrylate) in CH_2Cl_2 at 20 °C (Initiator: Methyl Triflate)

$[DXL]_0$, mol·L^{-1}	$[T]_0$, mol·L^{-1}	$[T]_e$,[a] mol·L^{-1}	$[I]_0$, mol·L^{-1}	M_n(calc)[b]	M_n(GPC)[c]	F[d]	M_w/M_n
6.35	0.337	0.059	0.0154	1542	1700	2.01	1.60
6.35	0.175	0.040	0.0090	2772	2500	1.80	1.85
6.35	0.155	0.036	0.0077	3269	3600	1.85	1.90
6.35	0.127	0.033	0.0064	4011	3800	1.79	1.80
bulk	0.440	0.029	0.022	5067	4300	1.87	1.95

[a] Determined by gas chromatography. [b] $74([DXL]_0 - [DXL]_e)/([T]_0 - [T]_e + [I]_0) + 272$. [c] Based on polyTHF standards. [d] Functionality calculated from ^{1}H NMR and GPC results.

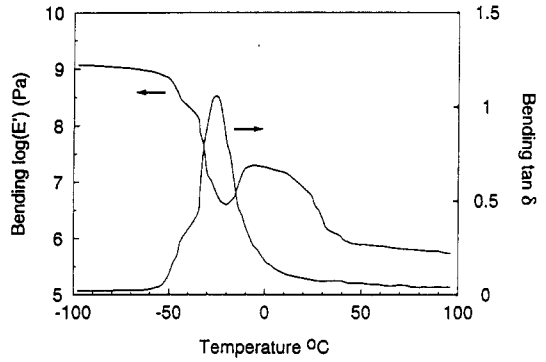


Figure 4. DMTA of a poly(BA-*g*-DXL) network (M_n(polyDXL) = 3000, [polyBA]/[polyDXL] (w/w) = 1, and frequency = 1 Hz).

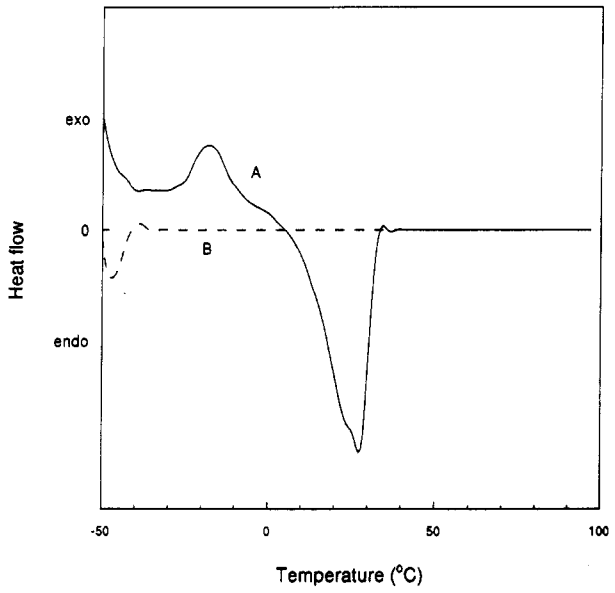


Figure 5. DSC analysis of polyDXL networks with polyMMA and polyBA segments: (A) poly(BA-*g*-DXL) ([polyBA]/[polyDXL] (w/w) = 1 and M_n(polyDXL) = 2700); (B) poly(MMA-*g*-DXL) ([polyMMA]/[polyDXL] (w/w) = 1 and M_n(polyDXL) = 3000).

Table II
Degree of Swelling of a 50/50 Poly(MMA-*g*-DXL) Network at 20 °C (M_n(polyDXL) = 3600, [MMA]/[polyDXL] = 20)

solvent	degree of swelling[a]	solvent	degree of swelling[a]
chloroform	1700	acetone	270
dichloromethane	1650	water	35
THF	650	methanol	34
toluene	460	pentane	0

[a] Expressed as $100(W_{swollen\ sample} - W_{sample})/W_{sample}$.

which the amounts of both reagents were so chosen that the polymerization mixture contained 5.3 mol % of macromonomeric methacrylate groups. The ^{1}H NMR analysis shows that the linear copolymer contains 4.9% of HEMA. In other words, more than 90% of the macromonomers have participated in the reaction. The molar mass of the linear copolymer was 31 000 g·mol^{-1}.

Table III
Degradation of a Poly(MMA-*g*-DXL) Network (M_n(polyDXL) = 3600, [polyMMA]/[polyDXL] (w/w) = 1)

solvent	$[H^+]$,[a] mol·L^{-1}	[OH],[b] mol·L^{-1}	T, °C	degradation time
CH_2Cl_2	10^{-2}	0	20	0.3 h
	10^{-2}	0.01	20	0.5 h
	10^{-2}	0.13	20	1.1 h
	10^{-2}	0.26	20	8.0 h
	10^{-2}	0.65	20	23.6 h
THF	10^{-2}	0.56	20	7 days
	10^{-2}	1.11	20	10 days
	10^{-2}	1.11	50	48 h
H_2O	1	55	20	>6 months

[a] CF_3SO_3H. [b] Isopropyl alcohol in CH_2Cl_2; water in THF.

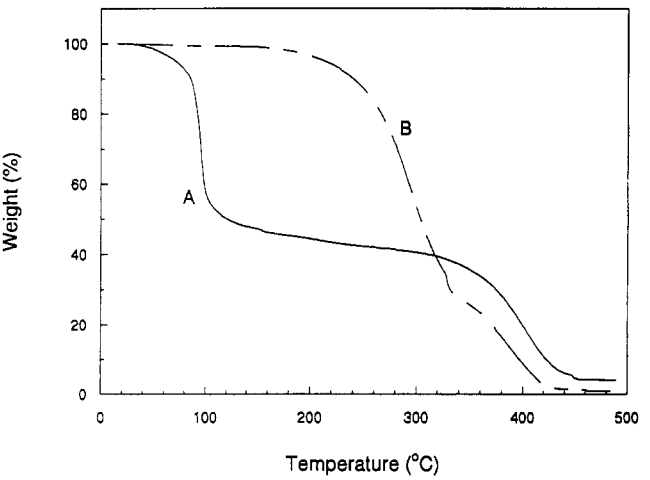


Figure 6. TGA of a poly(MMA-*g*-DXL) network ([polyMMA]/[polyDXL] (w/w) = 1 and M_n(polyDXL) = 3000): (A) acid-treated material; (B) untreated material.

Conclusion

It has been shown that the copolymerization of polyDXL bis(methacrylate) with other monomers leads to the formation of polymer networks. The physical properties of these materials can be changed by using different comonomers for the polymerization. Polymer networks containing polyDXL segments can be de-cross-linked under mild conditions by treatment with a trace of acid. Study of the degradation products shows that the cross-linking reaction with the polyDXL bis(methacrylate) reaches complete conversion. In the presence of alcohols and water de-cross-linking of the network can be prevented. However, the thermal stability of the acid-treated material is markedly lower than that of the untreated product.

Experimental Section

Products. 1,3-Dioxolane was purified by distillation over CaH_2 and dried on sodium wire under reflux in the presence of a trace of benzophenone until a blue color was obtained. The

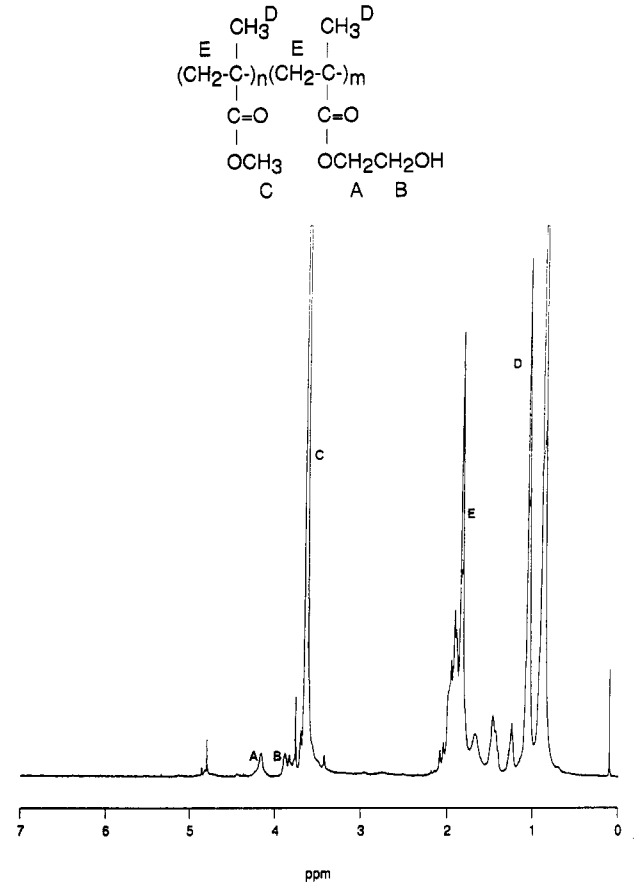


Figure 7. 360-MHz ^{1}H NMR spectrum of the soluble end product obtained by degradation of a poly(MMA-*g*-DXL) network.

monomer was distilled just before use (bp 74 °C). Dichloromethane was distilled twice over CaH_2 followed by drying under reflux on sodium–lead alloy for several hours. The solvent was stored in the dark and distilled just before use. Triethylamine was purified by distillation on tosyl chloride and dried by reflux on CaH_2. Methyl triflate was distilled over CaH_2 before use. Triflic acid was purified by distillation. Methyl methacrylate, 2-hydroxyethyl methacrylate, and butyl acrylate were purified by distillation in the presence of phenothiazine. Paraformaldehyde was used as received from Aldrich Chemical Co.

Synthesis of Methylenebis(oxyethyl methacrylate) (I). Amounts of 46.2 mL (0.36 mol) of 2-hydroxyethyl methacrylate, 6.61 g (0.21 mol) of paraformaldehyde, and 195 μL (22 mmol) of triflic acid are placed in a 100-mL flask provided with a magnetic stirring rod. The reaction mixture is stirred for 48 h at room temperature. The water formed during the reaction is removed continuously under vacuo. The triflic acid is neutralized by adding 3 g of poly(4-vinylpyridine-*co*-styrene). After 30 min of stirring, the polymer is filtered off, leaving 49 g of I. The compound can be distilled in vacuum [bp 140 °C (0.1 mm)], but this leads to a great loss in yield without a noticeable improvement in the purity.

Polymerization Procedure. Amounts of 4 mL (57.2 mmol) of DXL and 5 mL of CH_2Cl_2 are placed in a two-necked flask provided with a magnetic stirring rod, an inlet for dry nitrogen, and a glass neck equipped with a rubber septum. The reaction vessel is thermostated at 20 °C, and 7 μL (6.19×10^{-5} mol) of methyl triflate and 390 μL (1.43 mmol) of methylenebis(oxyethyl methacrylate) are introduced through the septum by means of a hypodermal syringe. The mixture is stirred for 3 h, and then 100 μL (7.2×10^{-4} mol) of triethylamine is added. The solution is poured into 100 mL of ether cooled to −116 °C by liquid nitrogen, and the precipitate is filtered off on a cooled G-3 sintered-glass filter. After washing with cold ether and drying under vacuo 3.52 g (yield 80%) of α,ω-bis(methacrylate)-terminated poly-DXL (II) with M_n = 3580 is obtained.

Network Synthesis in Solution. Amounts of 20 mL of toluene, 2 mL (19 mmol) of methyl methacrylate, 2 g (5.61×10^{-4} mol) of II (M_n = 3580), and 15 μg (9.35×10^{-5} mol) of 2,2′-azobis(2-methylpropionitrile) are placed in a glass tube. The mixture is degassed three times, sealed under vacuum, and then kept for 16 h at 70 °C. After removal of the solvent in vacuum 4.02 g of a glassy, rod-shaped end product is obtained.

Network Synthesis in Bulk. Amounts of 1.9 g (5×10^{-4} mol) of II (M_n = 3800), 1.8 mL (12.6 mmol) of butyl acrylate, and 62 mg (3.8×10^{-4} mol) of 2,2′-azobis(2-methylproprionitrile) are placed between two glass plates kept at 1-mm distance by a silicone rubber ribbon. The mixture is placed in an oven at 70 °C for 16 h. The glass plates can easily be removed, and 3.7 g of a transparent rubbery film is obtained.

Acid-Catalyzed Network Degradation. A typical network degradation procedure is as follows: 0.1 g of poly(MMA-*g*-DXL) (50/50, w/w) is added to 10 mL of a 0.01 M triflic acid solution in CH_2Cl_2 containing a certain amount of isopropyl alcohol. The degradation time is measured as the time necessary to dissolve the material completely.

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