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New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

38. New Networks from α,ω-Di(Methacryloyloxy)-Polyisobutylene

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Summary

A α,ω-di(methacryloyloxy)-polyisobutylene has been prepared in high purity and was crosslinked by heat or light. Heating to $\sim$95°C yielded $\sim$90% gel whereas illumination produced up to 80% gel. In the presence of AIBN gel formation was somewhat reduced. The swelling ratio of the network in benzene was much less than expected which indicates that an unusual network has formed.

Introduction

Syntheses by cationic techniques of various telechelic macromers, i.e., polymers carrying polymerizable end groups, schematically X-P-X, have recently been described; P = polyisobutylene (PIB) and X = vinyl (1), isopropenyl (2), epoxy (3,4), acrylate or methacrylate (5), and styryl or α-methylstyryl (6).

Earlier research from this laboratory demonstrated that a α-methacryloyloxy-polyisobutylene (polyisobutenyl methacrylate) macromer of $\overline{M}_n$ = 5200 (7) can be polymerized by free radical initiator to very high molecular weight products ($\overline{M}_v$ $\sim$6.8 x 10^5). Thus it appeared of interest to investigate the crosslinkability (polymerizability) of the corresponding telechelic macromers, i.e., a polyisobutylene carrying methacrylate MA functions on both ends MA-PIB-MA. The product promised to be an interesting new network.

This paper concerns a new and efficient method for the preparation of the α,ω-di(methacryloyloxy)-polyisobutylene (dimethacrylate-telechelic PIB) MA-PIB-MA and its crosslinking under the influence of heat or light to unusual new composite networks.

Experimental

A. Materials

The synthesis and purification of dihydroxy-telechelic PIB (HO-PIB-OH) has been described (8). Methacryloyl chloride was distilled before use. Triethylamine was used without purification. Methylene chloride, chloroform, n-hexane, benzene, and acetone were dried by Molecular Sieves. Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried in vacuo.

B. Procedures

The Snthesis of MA-PIB-MA

To 20g telechelic PIB-diol dissolved in 180 ml CH_2Cl_2 and 20 ml $CHCl_3$ was added 30 ml triethylamine. Then 15 ml freshly distilled methacryloyl chloride was added dropwise to the charge at 0°C under a nitrogen atmosphere, and the mixture was stirred overnight at room temperature. The solvents, triethylamine, and methacryloyl chloride were removed by a rotary evaporator and 50 ml *n*-hexane was added to the product. The solution was poured into an excess (∿500 ml) of acetone and the precipitation was repeated to remove completely triethylamine and methacryloyl chloride. The precipitate was dissolved in *n*-hexane and washed with methanol. A small amount of water was added to ascertain the separation between *n*-hexane and methanol. The *n*-hexane solution was dried over $MgSO_4$ and the product was recovered by evaporating the solvent. The telechelic macromers used in this study were stored in a refrigerator at 0°C. The functionality of the product was determined by ^1H-NMR spectroscopy (Varian Associates T-60 NMR). Details of the method and its accuracy have been described (5,7).

Crosslinking of MA-PIB-MA

MA-PIB-MA was crosslinked by the use of heat and/or light. The symbols I, II, III, and IV in Table I refer to the following methods, (I) Crosslinking by light: The sample was placed in a vial and AIBN was added. If necessary, benzene was added to obtain a homogeneous system; subsequently the solvent was removed by placing the vial in a vacuum oven at room temperature. The vial was placed into a water bath (25 ± 7°C) and was illuminated by a Sylvania Sun Lamp (275 W(125 V)) from a distance of ∿10 cm. (II) Crosslinking by heat: The sample in a vial was placed in a vacuum oven at 80 ± 5°C or 95 ± 5°C. AIBN was added and the system homogenized with benzene as described in (I). The solvent was removed in a vacuum oven at room temperature before heating. (III) The sample was stored in a vacuum oven at room temperature. (IV) The sample was stored in a refrigerator at 0°C.

Extractions

After heat or light treatments the samples wer extracted by *n*-hexane at room temperature for three days. The solvent was replaced every day. Gel fractions were determined gravimetrically before and after solvent treatment.

Swelling Experiments

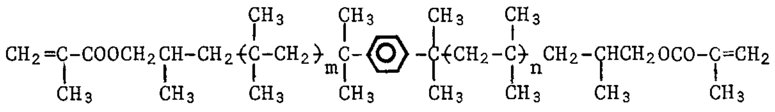
Swelling experiments were carried out using benzene at room temperature (9). Equilibrium swellings have been reached after a few days.

Results and Discussion

The first phase of this work was directed toward the efficient synthesis of MA-PIB-MA. The following equation helps to visualize the reaction employed:

$$\text{HO-PTB-OH} \xrightarrow[N(CH_2CH_3)_3]{CH_2{=}C(CH_3)COCl} \text{MA-PIB-MA}$$

The esterification method developed in this study is simpler and more efficient than the previously described methods (5,7). It employs inexpensive solvents (CH_2Cl_2 and $CHCl_3$) and catalyst ($N(CH_2CH_3)_3$), and the system is homogeneous since the triethylamine-acid complex is soluble in medium. The telechelic macromer



MA-PIB-MA

was a colorless transparent viscous liquid of number average functionality $(\overline{F}_n)$ 1.9 ± 0.1 by ^{1}H-NMR analysis (5,7), and $\overline{M}_n = 4200$ by GPC.

The results of crosslinking experiments are shown in Table I.

TABLE I

Formation of Gel by Heat or Light Exposures

Run	Macromer (g)	AIBN (g)	Crosslinking Method^a	Reaction Time(hrs)	Gel Fraction (wt.%)
1	0.4418	0	I	4	68
2	0.2771	0.0023	I	4	61
3	0.3668	0	I	10	81
4	0.2567	0.0038	I	10	78
5	0.6322	0	I	20	77
6	0.8093	0	II^b	22	87
7	0.1953	0.0025	II^b	24	77
8	0.7540	0	II^c	117	90
9	0.6513	0	II^c	195	89
10	0.3002	0	III	48	0
11	0.3300	0	III	120	18
12	$\sim$20	0	IV	>2 months	0

a) See Experimental

b) Heated to 80 ± 5°C

c) Heated to 95 ± 5°C

The MA-PIB-MA did not show evidence for gelation and its $\overline{F}_n$ did not change after storage for at least two months at 0°C in a refrigerator (run 12). In contrast, 18% gel was obtained after five days in vacuum at room temperature (run 11) (gel was absent after two days (run 10)).

Illumination of MA-PIB-MA in the bulk for 4, 10 and 20 hrs produced up to $\sim$80% gel (runs 1, 3 and 5) whereas in the presence of AIBN gel formation was somewhat reduced (runs 2 and 4). Essentially similar results have been obtained in experiments in which crosslinking was effected by heating to 80 ± 5°C (compare runs 6 and 7), although the level of gel formation was higher $\sim$87%. Indeed, the highest gel fractions $\sim$90% were obtained by heating to 95 ± 5°C (runs 8 and 9). According to ^{1}H-NMR spectroscopy the *n*-hexane-soluble fraction was MA-PIB-MA. Figure 1 shows the ^{1}H-NMR spectra of the starting material (A) and a representative *n*-hexane-soluble product after crosslinking (from run 1) (B).

Two questions arise: Since methyl methacrylate is readily polymerizable by light ($\lambda < 360$ nm) or by AIBN at moderately elevated temperatures, how come that crosslinking of MA-PIB-MA stops at 80-90%, and why does AIBN reduce the level of gel? The finite gel level may be due to the very high viscosity of the system at high gel contents, i.e., due to reduced diffusion the MA end groups of the telechelic macromer are unable to reach the propagating radical site. The fact that the sol fraction is unchanged MA-PIB-MA substantiates this proposition. Termination must be very slow in this system since according to our earlier investigations α-methacryloyloxy-polyisobutylene (polyisobutenyl methacrylate) macromer MA-PIB gives very high molecular weight polymer under essentially identical conditions (7). The effect of AIBN may be rationalized by assuming that this free radical source not only initiates the polymerization of MA groups and thus gives rise to crosslinking but also stops the propagation by radical recombination. The mobility of the small $(CH_3)_2C\dot{C}N$ radical most likely remains high even in the relatively viscous system.

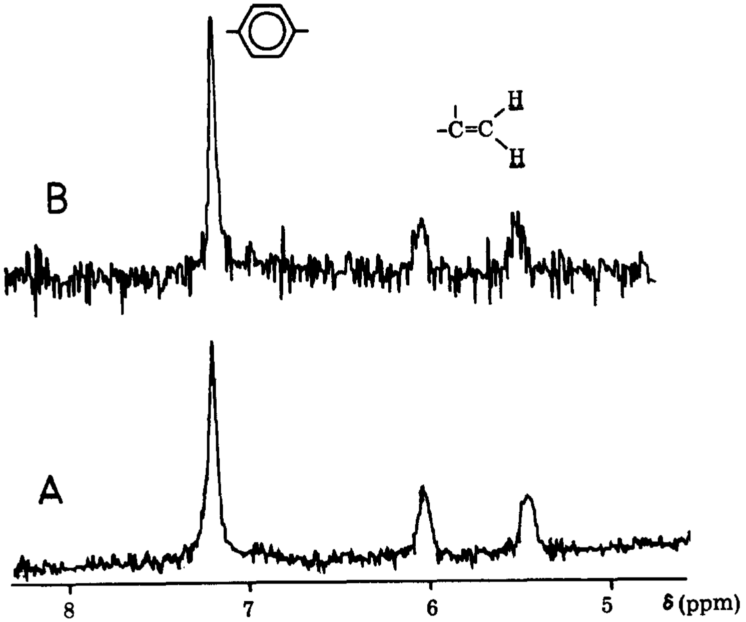


Figure 1. ^{1}H-NMR spectra of (A) the starting telechelic macromer ($\bar{M}n$ = 4200) and (B) the n-hexane-soluble product after light exposure (run 1)

Efforts have been made to characterize the networks by swelling measurements. The details of calculations have been described elsewhere (9, 10). The number of chains emanating from each crosslink (ϕ) was assumed to be large so that

$$v_{2m}^{1/3} - 2\, v_{2m}/\phi \approx v_{2m}^{1/3}$$

where v_{2m} is a volume fraction of polymer in the network at equilibrium swelling. The results are shown in Table II.

TABLE II

Swelling of Networks in Benzene at Room Temperature

Samples in Table I	Unswollen State weight(g)	Unswollen State volume(cm^3)	Weight(g) of Swollen Network	v_{2m}	$\bar{M}_c$ ^{a} (g/mol)
run 3	0.076	0.079	0.156	0.46	1300
run 8	0.141	0.16	0.278	0.49	1100
	0.164	0.17	0.331	0.47	1300
	0.575	0.58	1.164	0.46	1300

a) Calculated from the Flory-Rehner equation (10) and using χ_1 = 0.5 and v_1 = 89.37 cm^3/mol.

According to these data the $\overline{M}_c$ (i.e., molecular weight between crosslinking points) is much lower (∿1300 g/mol) than expected (4200 g/mol) indicating a very "tight" network. The crosslinked MA-PIB-MA's were colorless clear flexible sheets reminiscent of "overcured" rubbers (high initial modulus followed by rapid failure on manual stretching).

It is difficult to reconcile the swelling data with those of the extraction experiments. According to the latters the gel content of crosslinked materials was at best 90%, i.e., the networks could not have been tight; indeed a sol content of ∿10% would indicate the presence of substantial amounts of dangling chains (11).

In light of the structure of the telechelic macromer, the final network must consist of two components: polymethacrylate PMA chains and PIB chains. Since the network contains only ∿3% PMA, the continuous phase must be PIB. Phase separation between PMA and PIB probably exists, however, the PMA domains are most likely widely dispersed in the PIB matrix and their diameter is below the wavelength of visible light, since the sheets are optically clear. In view of the very low PMA content characterization by Tg has not been carried out.

The following model may help to visualize the composite network obtainable from MA-PIB-MA by free-radical techniques:

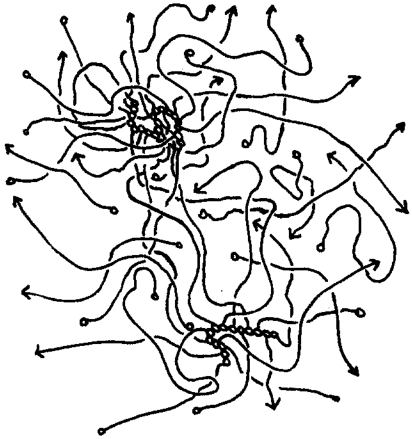


Figure 2. Model of the network obtained from MA-PIB-MA (o: MA group; ∿∿: PIB; ∿∿→: PIB connected to PMA domains)

The flexible rubbery PIB matrix is held together by PMA strands segregated into small domains in the hostile nonpolar medium. A large number of PIB chains is emanating from each PMA domain and the solvent (benzene) is unable to approach or penetrate these domains because of the extremely tight packing of the bulky PIB chains. Solvent exclusion should be significant in view of the large discrepancy between expected and observed swelling ratio.

Because of the simplicity of MA-PIB-MA synthesis and its crosslinking to clear flexible two component polar/nonpolar networks, these materials may be of interest as speciality adhesives, coatings, sealants, impermeable membranes, etc.

Acknowledgement

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