Polymer Bulletin 36, 27-34 (1996)

Polymer Bulletin

Polytetrahydrofuran macroinimer

Aysegul Baskan, Selcuk Denizligil, Yusuf Yagci

Istanbul Technical University, Department of Chemistry,
TR-80626 Maslak, Istanbul, Turkey

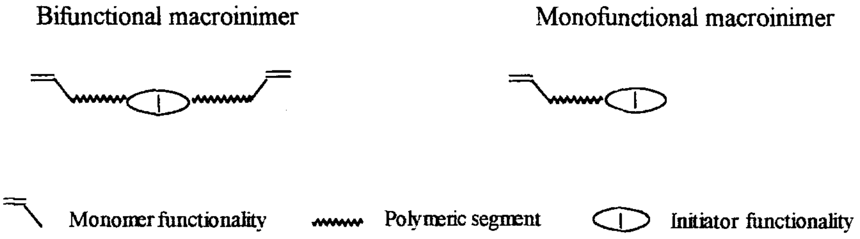
Received: 8 June 1995/Revised version: 14 August 1995/Accepted: 16 August 1995

Summary

Polytetrahydrofuran macroinimers were synthesized by means of cationic polymerization of tetrahydrofuran, initiated by azo-oxocarbenium salt, followed by termination with methacrylate anion. The macroinimers were characterized by ^{1}H-NMR analysis and GPC measurements. Self polymerization of macroinimers and copolymerization with methyl methacrylate (MMA) yielded crosslinked and soluble branched block copolymers depending on the MMA concentration.

Introduction

Recently, macromonomeric initiators refered to as macroinimers have been synthesized and applied to prepare block and graft copolymers and crosslinked networks (1). Macroinimer is a polymer molecule which possesses both monomer and initiator functionalities in the chain (Scheme 1).



Simplified structure of macroinimers

Scheme 1

In regard to the synthesis of macroinimers only few papers have been published to date. Hazer reported (2-4) the synthesis and radical polymerization of methacrylic and vinylic macroinimers obtained by the reaction of 4,4' azobis(4-cyanopentanoyl chloride) with excess polyethylene glycol (PEG) and followed by reaction with methacryloyl chloride and 4-vinyl benzyl chloride, respectively. The synthetic procedure requires two successive condensation reactions and condensation type reactions usually do not allow quantitative functionalization. Moreover, molecular weigth of the macroinimer is strictly related to the molecular weigth of the precursor PEG.

We have been much interested in macroinimers and have been planning a series of studies on the synthesis of thermal and photosensitive of macroinimers and their self polymerization and copolymerization with vinyl monomers. First of all, the preparation and polymerization of polytetrahydrofuran macroinimer (PTHF) were investigated. As it will be shown below, the macroinimer was prepared by the coupling reaction of living PTHF, initiated by azo-oxocarbenium salt, with methacrylate anions.

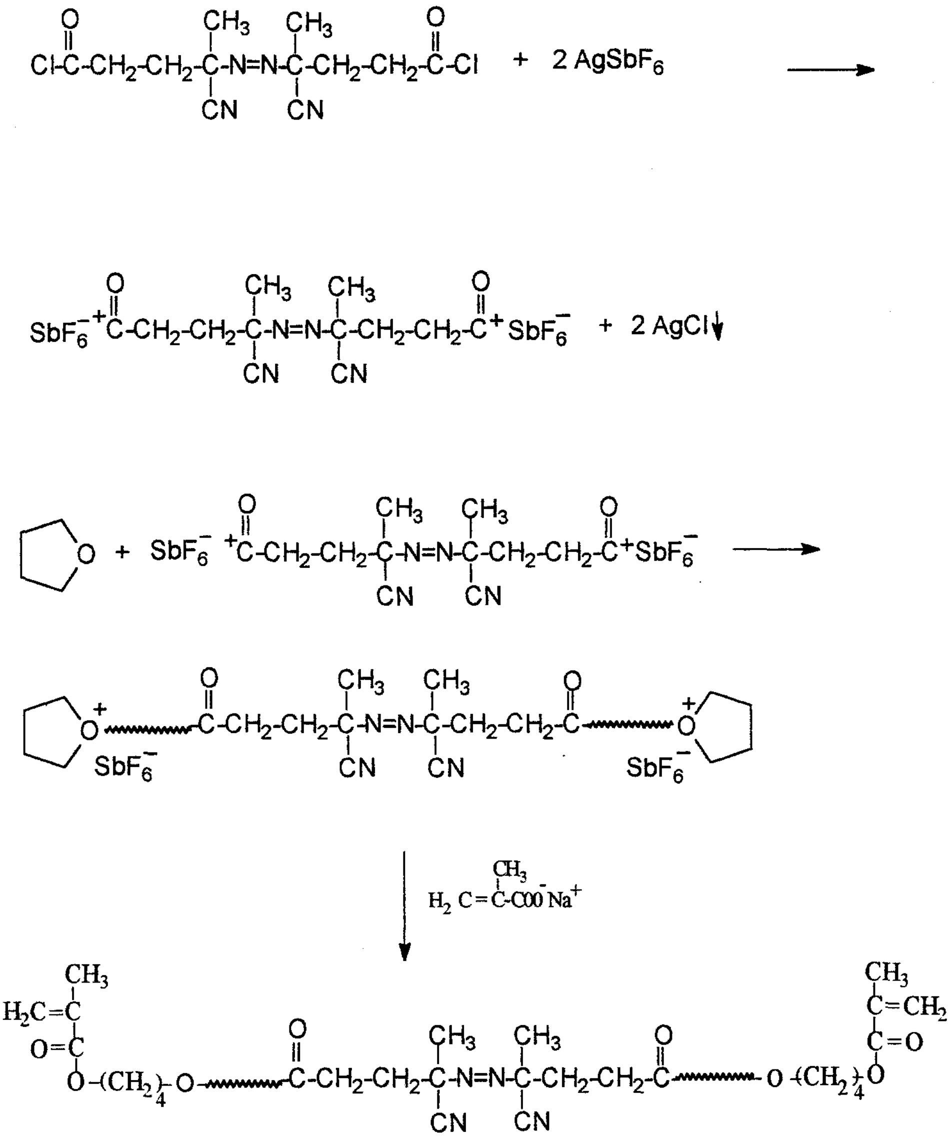
Experimental

Materials: Tetrahydrofuran (THF), methyl methacrylate (MMA) and methacrylic acid (MA), commercial grades were purified by conventional drying and distillation procedures. $AgSbF_6$ and 4,4-azobis(4-cyanopentanoic acid) (Fluka) were used without further purification. The corresponding diacid chloride (ACPC) was prepared according to a previously described procedure (5). Sodium methacrylate (6) was obtained by the reaction of sodium hydroxide with an excess of methacrylic acid in the aqueous solution and purified by the reprecipitation from methanol into excess acetone.

Synthesis of PTHF macroinimers: Living PTHF was prepared by the polymerization of THF initiated by azo-oxocarbenium salt according to the described procedure (7). At the end of given time, the polymerization mixture was added to an excess sodium methacrylate suspension in THF with stirring at 0^oC. The mixture was poured into a large amount of methanol / water (3/1 ,v/v) at 0^oC. The precipitated polymer was purified by reprecipitation from THF into water and dried.

Homo and copolymerization of PTHF macroinimers with MMA: Appropriate solutions of above obtained PTHF macroinimers alone or containing given amount of MMA in CH_2Cl_2 were made oxygen free with a nitrogen flow. At the end of heating in a thermostated bath at 60 ^oC for 60 minute, solutions were poured into methanol. Soluble and insoluble fractions were seperated by extracting with CH_2Cl_2.

Analysis of polymers: ^1H-NMR spectra were taken on a Bruker 200 instrument with solvent $CDCl_3$ and tetramethylsilane as the internal standard. Gel-permeation chromatography (GPC) analyses were performed with a set up consisting of a Water pump (model 600E) and three Ultrastyragel columns with porosities, 10^4, 500 and 100 A^o, respectively. THF was used as eluent at a flow rate of 1mL/min and the detection was achieved with a Waters differential refractometer (model 410). Samples were injected by using a 20 μL sample loop. Polymer concentrations were in the range of 2 to 3 g/100 mL. Molecular weights were calculated with the aid of PTHF standards.



Synthesis of polytetrahydrofuran macroinimer

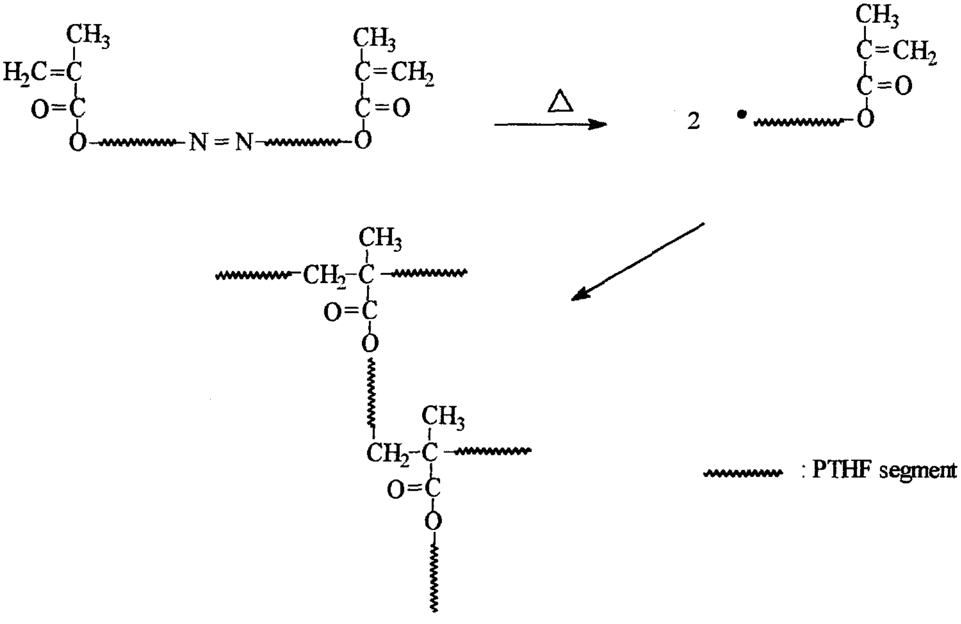
Scheme 2

Results and Discussion

We have previously shown (8) that the initiation of THF polymerization by azo-oxocarbenium salt is quantitative, rapid and proceeds by an addition mechanism. We have already reported the synthesis of block copolymers possesing PTHF and vinyl (9) or liquid crystalline (10) segments using azo-oxocarbenium initiator and more recently prepared PTHF initiator for sequential photochemical and thermal initiation by the reaction of living PTHF with *N*-oxides (11). In this work, we employed the same initiator for the polymerization of THF. PTHF macroinimers were prepared by nucleophilic substitution of the living ends of the polymer with sodium methacrylate according to Scheme 2. The S_N reaction of an oxonium end group with sodium methacrylate was reported (6) to proceed fast and quantitatively.

Table1 shows the results of the synthesis of PTHF macroinimers. The macroinimers obtained were charactarized by ^{1}H-NMR analysis and GPC measurements. The ^{1}H-NMR spectrum of a typical macroinimer in Figure 1 exhibits weak signals at 5,6 and 6,2 ppm corresponding to vinylic protons in addition to the characteristic PTHF signals. The molecular weight (M_n:22500), which was determined from the integration ratios, of the signals was in good agreement with that by the GPC method (M_n:21000). This result indicates that the macroinimer obtained by this method was highly pure and possesess two vinyl groups per macromolecule (C = C :1,9).

Molecular weight distribution of PTHF macroinimers is rather low (see Table 1). Macroinimers were thermally homo and copolymerized with methylmethacrylate (MMA) in CH_2Cl_2 at 60 ^oC. As can be seen from Table 2 both macroinimers yielded only crosslinked products in the absence of MMA, since macroinimers possess both initiating and polymerizing functionalities. Polytetrahydrofuran macroradicals formed upon thermolysis react with polymerizable acrylate to the following reaction (Scheme 3).



Scheme 3

Table 1. Synthesis of PTHF macroinimers

	Living PTHF			Coupling				
Denotation	ACPC (mol.l^{-1})	$AgSbF_6$ (mol.l^{-1})	Time (min)	[Na-MA] / $[O^+]$[a]	Time (min)	Yield (%)	M_n[b]$\times10^{-3}$ (g mol^{-1})	Mw /Mn
PTHF-1	7×10^{-2}	14×10^{-2}	30	2,13	60	32,1	21	1,2
PTHF-2	14×10^{-2}	28×10^{-2}	30	1,75	60	25,5	5,4	1,3

[a] Concentration of living oxonium ion
[b] Determined by GPC

Table 2. Homopolymerization and copolymerization of PTHF macroinimers with MMA in CH_2Cl_2 at 60°C for 60 minutes.

Run	PTHF macroinimer (g / l)	MMA (mol.l^{-1})	Conversion[a] (%)	Crosslinked Products (%)	PTHF[b] (%)
1	PTHF-1 (100)	–	–	100	
2	PTHF-1 (100)	1,9	2,2	97,2	95[c]
3	PTHF-1 (100)	4,7	23,9	87,8	9[d]
4	PTHF-1 (100)	7,5	12	38,6	
5	PTHF-1 (28)	23	57,2	–	
6	PTHF-2 (100)	–	–	100	
7	PTHF-2 (100)	1,9	51,2	89,3	54[c]
8	PTHF-2 (100)	4,7	51,8	49,1	28[d]
9	PTHF-2 (100)	7,5	36,3	32,1	
10	PTHF-2 (28)	23	70,9	4,5	

[a] Overall conversion of MMA
[b] Determined by elemental analysis
[c] Soluble fraction
[d] Insoluble fraction

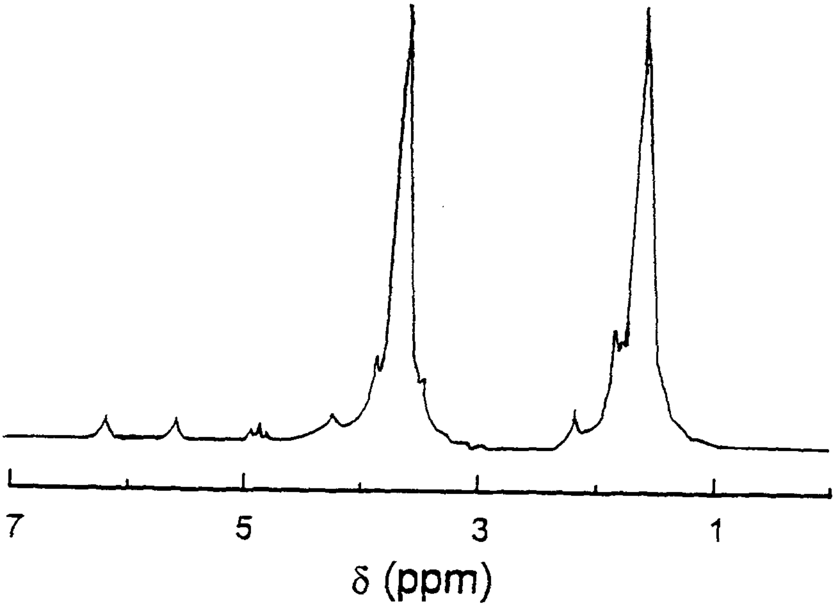


Figure 1- ^{1}H-NMR spectrum of PTHF-1 macroinimer

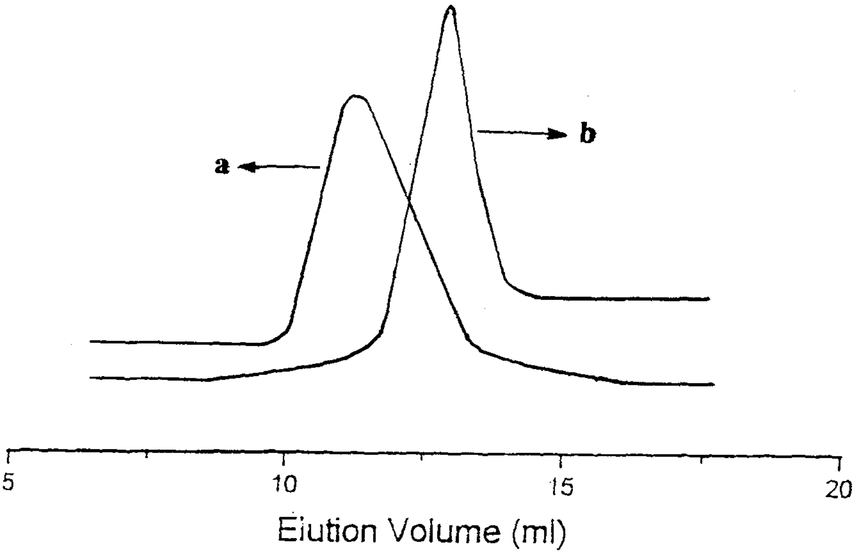


Figure 2- GPC curve of (a) the soluble fraction of branched MMA-THF block copolymer (Run 3 in Table 2) and (b) PTHF-1 macroinimer

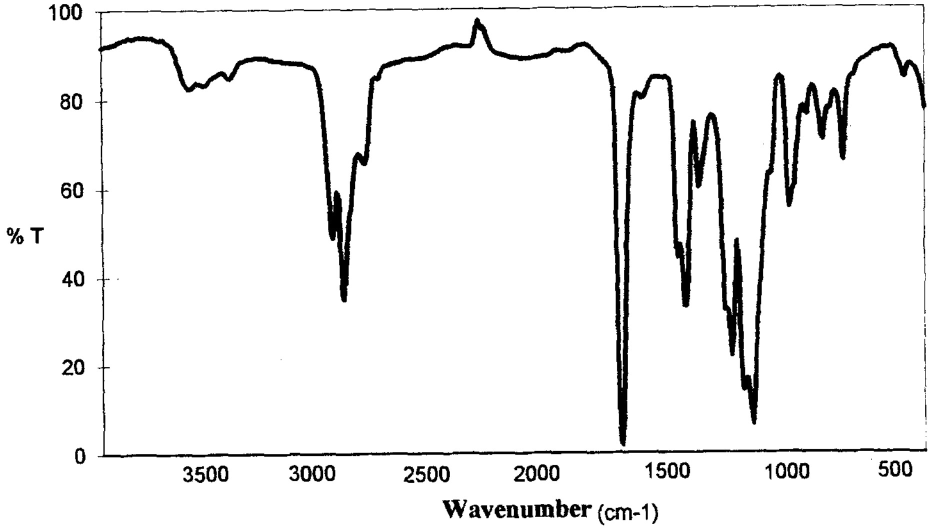


Figure 3- IR spectrum of the soluble fraction of branched MMA-THF block copolymer (Run 3 in Table 2)

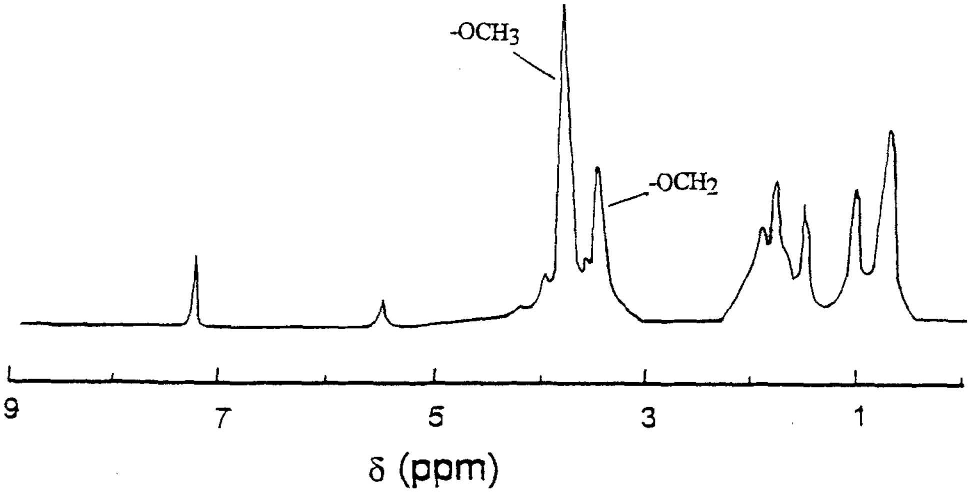


Figure 4- ^{1}H-NMR spectrum of the soluble fraction of branched MMA-THF block copolymer (Run 3 in Table2)

Polymerization of MMA with macroinimers gave branched and crosslinked MMA-PTHF block copolymer. Soluble fraction of the products increased with increasing monomer concentration. Notably, a control experiment without PTHF macroinimer failed to produce any precipitable polymer after the same heating time at 60^oC. Both soluble and crosslinked block copolymers possess PTHF segments. Notably, the percentage of PTHF segment is high in the crosslinked product whereas soluble polymers contain mainly PMMA segments (see Table 2). The precursor PTHF macroinimers dissolve in methanol at room temperature and precipitate at low temperature, i.e. 0^oC. The temperature dependent solubility behaviour of low molecular weight PTHFs makes it possible to separate resulting block copolymers from precursor macroinimer. Figure 2 shows GPC traces of the initial PTHF-1 macroinimer and of block copolymer precipitated at room temperature. It is interesting to note that block copolymer fraction does not contain residual initiating polymer. In Figure 3 , the FT-IR spectrum of the soluble branched THF-MMA block copolymer exhibits bands characteristics of carbonyl group of PMMA at 1730 cm^{-1} and of ether group of PTHF at 1190 cm^{-1}. These findings were further supported by ^{1}H-NMR analyses of the block copolymer obtained. The ^{1}H-NMR spectrum of the same polymer (Figure 4) displays signals corresponding to $-OCH_3$ protons at 3,6 ppm and to $-OCH_2$ protons at 3,4 ppm indicating the existence of both THF and MMA segments.

The study on the preparation of photosensitive macroinimers will be undertaken.

Acknowledgement

The authors gratefully acknowledge the financial support from ITU-Arastirma Fonu and Tubitak which generously provided an MSc scholarship for A.Baskan.

References

1. Mishra, M.K., Yagci,Y. (1994) in Macromolecular Designi Concept and Practice, (Mishra, M.K. Ed.), Polymer Front. Int'l Inc., New York, Chapter 14, pp. 449-506.
2. Hazer, B.,(1992) Makromol. Chem.,193,1081
3. Hazer, B., (1991) Macromol Rept. A28 (Suppl. 1) ,47
4. Hazer, B., (1993), J.Appl. Polym. Sci.,47,1097
5. Yagci, Y.,(1985), Polym.Commun., 27,25
6. Takaki, M., Asami,R., Kuwabara, T.,(1982) Polym. Bull.,7,521
7. Hizal, G., Yagci,Y., (1989) Polymer, 30,722
8. Serhatli,I.E., Hizal,G., Yagci,Y., (1992), Turk. J.Chem. 16,91
9. Galli,G., Chiellini,E.,Yagci,Y., Serhatli,I.E., Laus,M., Bignozzi,M.C.,Angeloni,A.S. (1993) Makromol. Chem., Rapid Commun. 14,185
10. Denizligil,S., Baskan,A., Yagci,Y.,(1995), Macromol. Rapid Commun, 16, 387