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Transformation of Cationic Polymerization of Tetrahydrofuran into Anionic Block Copolymerization of Methyl Methacrylate

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Summary

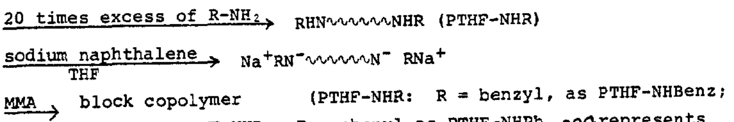
A new approach has been developed to transform the cationic polymerization of tetrahydrofuran (THF) into anionic block copolymerization of methyl methacrylate (MMA). Several telechelic polytetrahydrofurans with secondary amine end-groups (PTHF-NHR, where R = benzyl, n-butyl or phenyl) have been synthesized. The PTHF-NHR, where R is a phenyl group, can be almost completely metallated by sodium naphthalene to form the polymeric anion which will initiate quantitative polymerization of MMA to form a block copolymer, poly(MMA-b-THF-b-MMA), exhibiting thermoplastic elastomer properties of tensile strength 157kg/cm^2 and elongation 700%.

Introduction

According to the literature several attempts have been made to prepare block copolymers of tetrahydrofuran (THF) with other monomers by switching the mechanisms of polymerization (PENCZEK 1979; HAWARD 1979), but little is known about the conversion of a cationic polymerization into anionic one.

SUZUKI et al. (1980) succeeded in obtaining an ABA type block copolymer by anionic polymerization of MMA using the sodium amide of the telechelic oligomer of polyethylene oxide with benzyl amine end groups (PEO-N). These authors prepared PEO-N (MW 4000) in two steps by tosylation followed by aminolysis with benzyl amine.

We have already reported that the bulk polymerization of THF initiated by sebacoyl chloride (SC)-AgClO$_4$ at 0°C and -10°C will give a dicationic living polymerization (ZHANG and FENG 1981). This paper reports a new approach to transform this dicationic polymerization of THF into anionic block copolymerization of MMA according to the following scheme:



(PTHF-NHR: R = benzyl, as PTHF-NHBenz; R = n-butyl, as PTHF-NHBu; R = phenyl as PTHF-NHPh. ∿∿ represents the PTHF chain.)

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Experimental

1. Synthesis of PTHF-NHR (SMITH and HUBIN)

The living dicationic PTHF was prepared at -10° - 23°C by a technique described in our previous paper (ZHANG and FENG 1981). The clean solution of PTHF dications was transfored into the amines. After distilling out the THF and terminating agent in vacuum, 5-20 ml of 5% KOH-methanol solution was added (for PTHF-NHPh, the product was treated with 5-20 ml of 5% HCl-methanol solution, washed with water 5 times and dissolved in 10-40 ml of THF and then the alkali solution was added). The solution of the product was poured into a large amount of water. After evaporating the THF in vacuum, the product was washed with water 5 times, dissolved in cyclohexane and decolorized by activated carbon. After evaporating the cyclohexane and drying at 60°C under reduced pressure, a white waxy PTHF-NHR was obtained.

2. Block copolymerization and model experiment

To 1g PTHF-NHR freeze-dried from benzene (for the model experiments the amines were used directly), 10 ml THF was added by syringe. The system was evacuated for 1 min. at 0°C and purged with pure nitrogen. Then it was titrated with a 0.2 - 0.5N sodium naphthalene-THF solution at 0°C by a syringe until the color of sodium naphthalene remained stable. The MMA was quickly injected while vigorously stirring at 25-30°C. Then the reactant was poured into 500 ml of water (acidified with HCl, pH = 1). After evaporating the THF under reduced pressure, the product was filtered, washed 5 times with water, and dried at 60°C for 12 hrs. under vacuum.

Results and Discussion

1. Preparation and analysis of PTHF-NHR

TABLE I. The Analytical Results of PTHF-NHR and PTHF-OPh

PTHF-NHR	$[SC] \times 10^2$	Convn.	Eq. of endgroup $\times 10^{-3}$			$\bar{M}n \times 10^{-3}$	
	$(mol \cdot l^{-1})$	of THF (%)	Amino group[a]	Benzyl group[b]	Phenoxy group[c]	Calc.[d]	By VPO[e]
PTHF-OPh	8.89	45			2.1	4.5	4.3
R=Benz	8.89	45	2.9	2.3		4.5	4.4
R=Benz	8.89	45	2.8	2.4		4.5	4.2
PTHF-OPh	8.89	54			2.9	5.4	5.7
R=Benz	8.89	54		2.5		5.4	5.2
PTHF-OPh	8.82	40			1.8	4.0	3.7
PTHF-OPh	2.67	18.5			3.7	6.2	6.1
R=Bu	2.67	18.5	3.5			6.2	
R=Benz	2.67	27	4.6	4.5		9.0	
R=Ph*	3.03	32	4.6[f]			9.5	
R=Ph	3.03	43		6.3		12.7	

[a] by $HClO_4$-CH_3COOH non-aqueous solvent conductivity (SMITH and HUBIN). [b] by UV spectroscopy, n-butyl benzyl amine in cyclohexane shows $\lambda_{max.}$ at 214 mμ with $\varepsilon_{max.} = 4.80 \times 10^3$ l/mol.cm. [c,d] according to SAEGUSA and MATSUMOTO (1968), and

$$\bar{M}n(\text{calc.}) = \frac{\text{Wt. of polymer}}{(SC)} \times \frac{1}{\text{volume of system}}.$$

[e] determined in $CHCl_3$ at 35°C. [f] by titration with sodium naphthalene-THF solution. *MWD = $\bar{M}w/\bar{M}n$ = 1.3, by GPC (Fig. 1).

According to the analytical results (Table I) of PTHF-NHR and PTHF-OPh (with two phenoxy end-groups) prepared by terminating PTHF dications with large excess (five times) of 0.5N sodium phenolate, the functionality (f = $\bar{M}$n/equivalent of end-group) is close to 2.

2. Model metallation reaction

In order to study the reactivity of PTHF-NHR toward the metallation reaction by sodium naphthalene, several amines, such as n-butyl benzyl amine, di-n-butyl amine and N-methyl aniline were used as model compounds to form PHTF-NHBenz, PTHF-NH-Bu and PTHF-NHPh, resp.. In addition, the PTHF-OPh($\bar{M}$n = 9500) was used simultaneously for comparison. MMA was then polymerized by these sodium amindes. The reactivity of the model amines shows the following sequence (Table II):

N-methyl aniline (100%)>>di-n-butyl amine (40%)∿n-butyl benzyl amine (29%).

These results are in agreement with the order of basicity of amines.

TABLE II. Metallation Reaction of Model Amines and Polymerization of MMA

Model amine	Amount of amine x10^3 mol.	V_1 (ml.)	V_2 (ml.)	V_3 (ml.)	Degree of metallation		
					by $\frac{V_1}{V_2}$*	by bonded N in PMMA	by GC**
n-butyl benzyl amine	0.706	0.4	1.4	1.9	29	<37	35
di-n-butyl amine	0.754	0.6	1.5	2.0	40	<37	50
N-methyl amine	0.640	1.3	1.3	1.8	100	73	87

For metallation, 0.30g PTHF-OPh was added; polymerization (1.0 ml MMA) was carried out at 27°C for 12 hrs.; conversion of MMA was about 100%. V_1, V_2, and V_3 represent the volume of 0.5N sodium naphthalene in titration until the color appeared, the volume calculated for the complete reaction of metallation, and the volume used, resp.. *According to TAKAKI et al. (1981). **Calculated by the amount of unreacted amines after polymerization. GC (102 G type, China), fitted with OV-17, column temperature 190°C for n-butyl benzyl amine and 160°C for other amines, hydrogen flame detector.

3. Block copolymerization of MMA initiated with sodium amide of PTHF-NHR at room temperature

As shown in Table III, a thermoplastic elastomer (TPE) with tensile strength 157 kg/cm^2 and ultimate elongation 700% was obtained only with PTHF-NHR where R = Ph. While the product was extracted by warm petroleum ether (boiling range 30-60°C) the soluble part (only 2-3%, Table III) contains not only PTHF segments, but also 31% MMA units, indicating that almost all the polymeric initiator employed was incorporated into the block copolymer. The GPC traces of B-12 and PTHF-NHPh (Figure 1) provide the same conclusion. Fractions obtained from 5% acetone solution of the extracted sample of

B-12 at 26°C by petroleum ether behaves quite differently from fractions obtained from the mixture of the two homopolymers (Figure 2). ^{1}H NMR spectroscopy shows that the highest MW fraction (precipitate b) consists of MMA and PTHF in the ratio of 56 to 44 and homo-PMMA is absent.

These observations together with the use of dianionic polymeric initiator formed due to the complete metallation reaction of PTHF-NHPh, and the TPE properties of the products confirm the formation of PMMA-PTHF-PMMA triblock copolymers. The existence of the peak at extremely high MW in GPC traces may be explained by the formation of some branched or extended chains in the copolymer. Further studies are in progress.

TABLE III. Block Copolymerization of MMA Initiated by Sodium Amide of PTHF-NHR at room temperature

NO	PTHF-NHR R	PTHF-NHR Mn x 10^{-3}	W_{MMA} (wt.%)	Convn. of MMA (%)	Extract wt.%	Extract MMA unit (wt.%)	product
B-6	benzyl	9.0	71	100	10	0*	rigid powder
B-8		9.0	40	100	10	trace**	gum like
B-10		6.2	40	100			soft powder
B-11		9.5	45	100	14	a little**	leather like
B-5	n-butyl	6.2	70	100	7	trace	rigid powder
B-7		6.2	41	100	9		gum like
B-31		9.5	45	85	16		soft powder
B-12	phenyl	9.5	49	100	2	31*	TPE
B-13		9.5	46	100	3		TPE

Copolymerization was carried out at 25-30°C/15-30 min. and 12-22°C/12-14 hrs.. W_{MMA} represents the charge of MMA. *by ^{1}H NMR: $\delta_{(-OCH_2-)}$ 3.41 ppm; $\delta_{(-COOCH_3)}$ 3.60 ppm. **by IR: -CO-1720 cm^{-1}, -COOCH$_3$ 1135 cm^{-1} and 1190 cm^{-1}; -COC-1110 cm^{-1}.

In case of PTHF-NHBenz or PTHF-NHBu, a significant amount of starting polyether was recovered by extracting with petroleum ether (Table III). The GPC traces of B-11 and B-5 also show a partial overlap with traces of the starting polyethers. These results correspond with the incompleteness of the metallation of PTHF-NHBenz and PTHF-NHBu. Thus the products obtained in such copolymerizations do not exhibit TPE properties and contain both triblocks and diblocks.

4. Characterization of the thermoplastic elastomer block copolymer B-12

The DSC curve (Figure 3) of the block copolymer B-12 showed a Tg (-54°C) and a Tm (30°C) corresponding to the PTHF matrix. The viscoelastic spectra (Figure 4) of B-12 (0.5 mm thick specimen casted from 10 wt.% solution of THF) indicated the Tg$_1$ (-75°C) and Tg$_2$ (77°C) corresponding to the PTHF matrix and PMMA domains, respectively, and the rather high elastic modulus (10^8 dyne/cm^2) below 30°C indicates partial crystallization of the PTHF matrix resulting in a lack of rubber elasticity. A thawed specimen of B-12 remained elastic after storage for one year at room temperature.

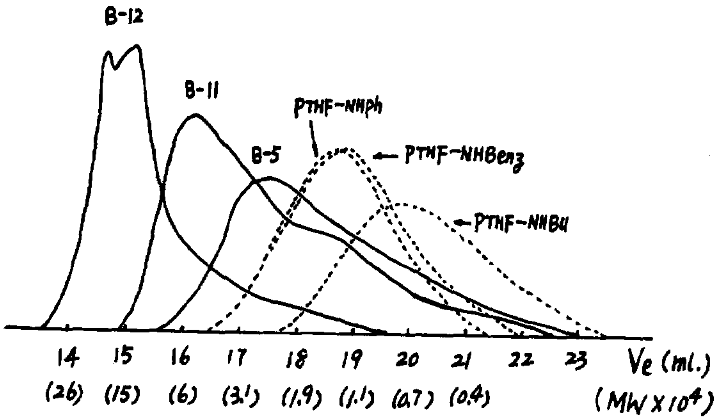

Fig. 1. The GPC traces of block copolymers.
Determined by Waters ALC/GPC 244 with µ-styragel columns (10^4 +10^3+500 A); THF as the eluent (1.0 ml/min.); MW was calibrated with standard polystyrene. RI 16x. B-12, B-11 or B-5 represents the block copolymer of PMMA and PTHF-NHPh, PTHF-NHBenz or PTHF-NHBu, resp..

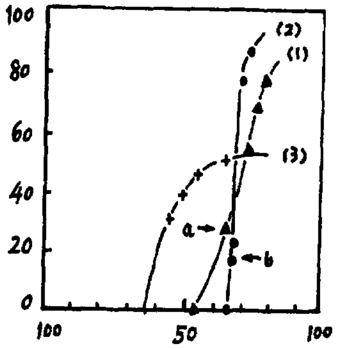

Fig. 2. Fractional precipitation curves of block copolymers.

(1) B-11; (2) B-12; (3) mixture of 52 wt.% PMMA (MW 20,000) and 48 wt.% PTHF-NHBenz ($\bar{M}n$ = 9,500).

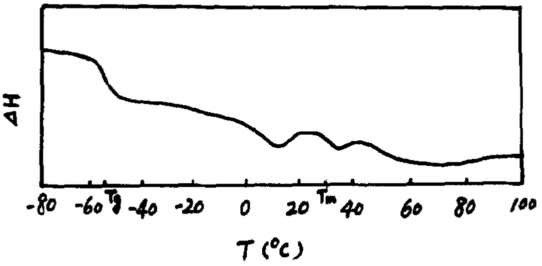

Fig. 3. DSC curve of the block copolymer B-12, by DuPont 9900 DSC. 5°C/min.; 2 mcal./sec.

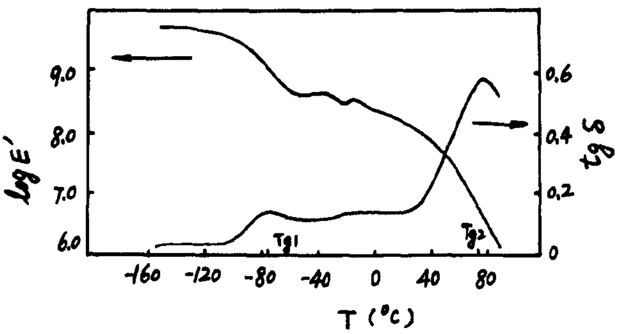

Figure 4. Viscoelastic spectra of the block copolymer B-12

Tg (-54°C) and a Tm (30°C) corresponding to PTHF matrix. The viscoelastic spectra (Fig. 4) of B-12 (the specimen with 0.5mm thickness was casted from 10 wt.% solution of THF) indicated the Tg_1 (-75°C) and Tg_2 (77°C) corresponding to the PTHF matrix and PMMA domains, respectively, and the rather high elastic modulus (10^8 dyne/cm^2) below 30°C illustrated the partial crystalization of the PTHF matrix resulting in the lack of rubber elasticity. But the unfreezed specimen of B-12 retains the rubber elasticity after storage for one year at room temperature.

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