

Block Copolymers by Combination of Cationic and Radical Routes: 6. Synthesis of Tetrahydrofuran-Vinyl Block Copolymers*

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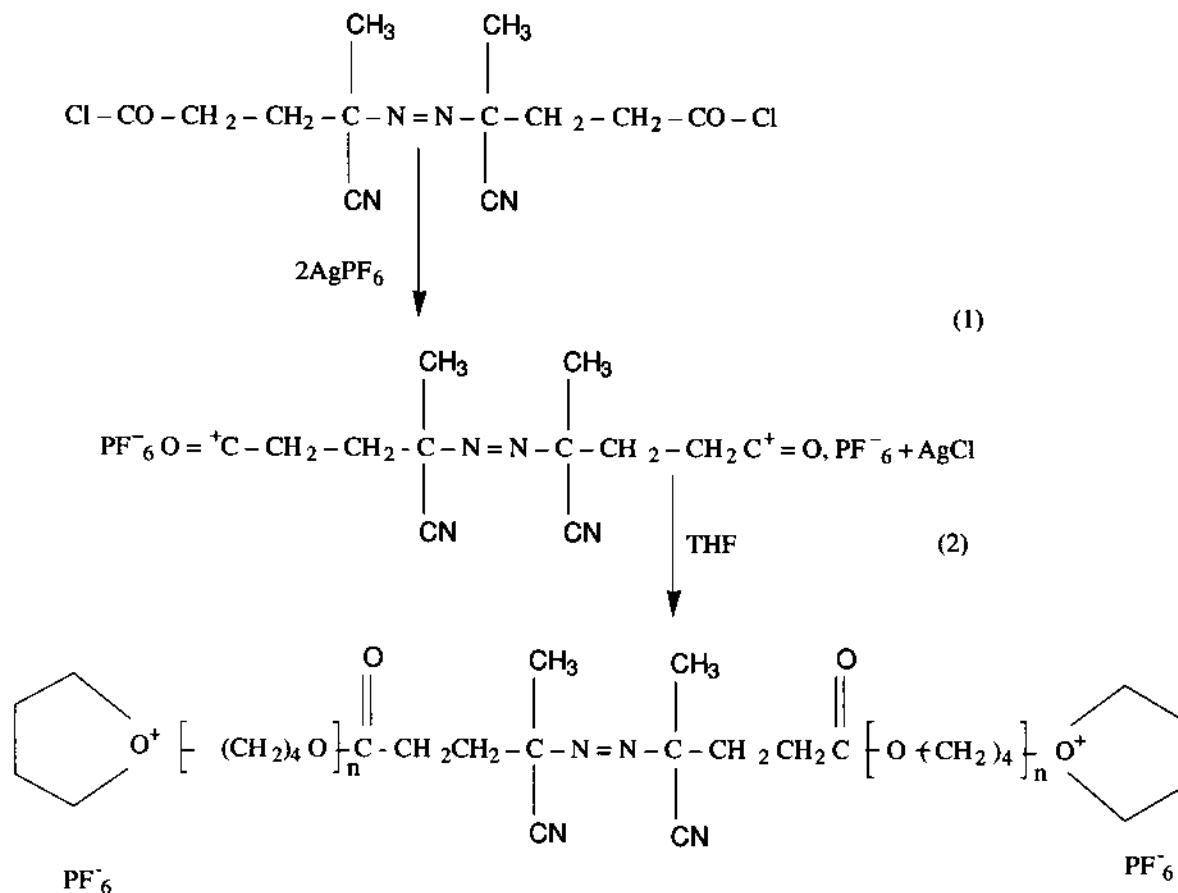
Polytetrahydrofuran with a thermo-sensitive group was prepared by reacting 4,4'-azo bis (4-cyanopentanoyl chloride) with $AgPF_6$ in the presence of tetrahydrofuran. These polymers were used to induce the radical polymerization of various vinyl monomers through the thermal decomposition of the azo group, resulting in the formation of poly (tetrahydrofuran-b-vinyl) copolymers.

Introduction

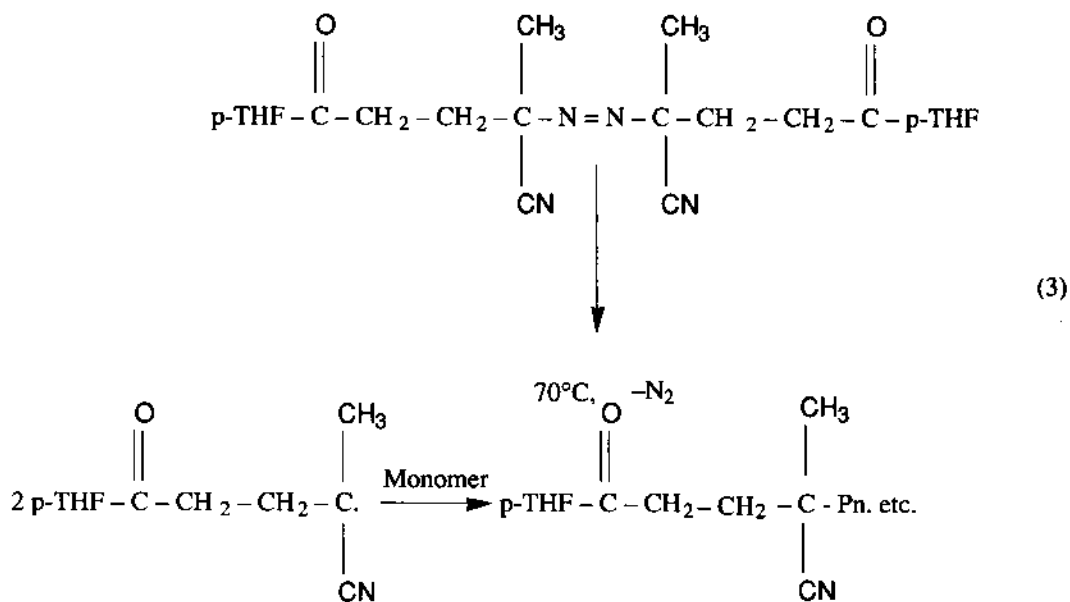
Block copolymers that contain poly (tetrahydrofuran) (PTHF) segments are of interest.¹

Incorporation of soft PTHF blocks into conventional vinyl polymers should lead to polymers with the desired physical properties. It is well known that tetrahydrofuran (THF) is a nucleophilic monomer and polymerizes by the cationic mechanism. Cationic polymerization is limited to certain types of vinyl monomers and excludes the possibility of preparing block copolymer of THF with other monomers that polymerize by other mechanisms. Additionally, contamination of homopolymers can not be prevented since chain transfer reactions dominate cationic polymerization of vinyl monomers. Richard^{2,3} proposed an elegant method that allows combination of THF with monomers. In this approach, polystyrene, prepared anionically, is terminally functionalized, isolated and subsequently used to initiate the polymerization of THF cationically to form block copolymers. Similarly, Abadie et al⁴ described block copolymerization of THF with vinyl monomers by transformation of radical centers into cationic centers. Previously, we presented a new approach of preparing block copolymers by cation to radical^{5,6} and reverse^{7,8} transformation polymerization. This approach is based on the use of a bifunctional low-molecular weight initiator containing acid-chloride end groups and an azo-group. The most effective usage of this initiator was made by reacting acid chloride groups with non-nucleophilic silver salts in the presence of THF and subsequent thermal decomposition of the azo-group in the presence of styrene (St).

* For part 5 of this series, see Polymer 31, 1803 (1990)



Since the azo group is contained in the main chain of the polymer formed in the first step, a block copolymer is obtained in the second step.



In this paper, we will thoroughly demonstrate the use of azo-linked pTHF for initiating polymerization of viny monomers, namely styrene (St), methylmethacrylate (MMA), ethylacrylate (EA), and acrylonitrile (AN), which results in the formation of THF and corresponding vinyl block copolymers.

Experimental

Materials

All monomers and solvents were purified by conventional drying and distillation procedures. A_gPF_6 and 4,4' azo bis (4-cyanopentanoic acid) (Fluka) were used as purchased. The corresponding acid chloride (ACPC) was prepared according to a procedure described elsewhere.⁹ Polytetrahydrofuran (PTHF) containing azo-linkage were prepared as described previously.¹⁰

Block copolymerization of pTHF with viny monomers

Appropriate solution of viny monomer in THF containing a given amount of active pTHF were outgassed in the usual manner and placed in a thermostat at 70°C.

At the end of polymerization, the reaction mixtures were poured into ten-fold excess of methanol and the precipitated polymers filtered and dried. Block copolymers were freed from homo PTHF by extracting with ethanol.

Analysis

$^1H - NMR$ spectra were recorded on Bruker AC 250 spectrometers using TMS as the internal standart. IR spectra were recorded on a Jasco FTIR 5300 spectrometer. Molecular weights of polymers were determined from G.P.C. chromatograms according to standard polystyrene using a Knauer M-64 instrument and THF as the eluent at a flow rate of 1ml/min.

Results and Discussion

PHF, containing a labile azo group in the main chain were prepared by reacting diacid chloride with silver salts (eqs.1-2). Polymerization conditions and results are shown in Table 1. In part 4 of this series it was shown¹⁰ that polymerization proceeds without termination and PTHF obtained via this initiation method contained one azo-linkage per macromolecular chain.

Table 1. Preparation of polytetrahydrofuran with azo group,
 $[THF] = 12, 3mol.l^{-1}$, $[ACPC] = 4, 5.10^{-2}mol.l^{-1}$, $[AgPF_6] = 9.10^{-2}mol.l^{-1}$, $Temp = 0^\circ C$

Run No	Time (min)	Conversion (%)	$\overline{M}_n^a \cdot 10^{-3}$ (g/mol)	$\overline{M}_w/\overline{M}_n$
1	35	11	34.0	1.17
2	80	37.5	66.0	1.10
3	110	42	82.0	1.57

^aDetermined by G.P.C. measurements.

With the aid of this polymer, block copolymers of THF can be obtained by the method proposed previously, the polymer is heated at 70°C in the presence of vinyl monomer. PTHF attached radicals can start the polymerization of a viny monomer which is contained in the system according to reaction 3. Typical results concerning block copolymerization of PTHF with various vinyl monomers are shown in Table

2. Notably, the molecular weight and concentration of thermo-labile PTHF and polymerization time affect the conversion and composition of block copolymer. It is also interesting to note the higher yields in the case EA and AN which may be attributed to the polymerizability of the related monomers.

The block copolymer composition has been determined in several examples by ^1H-NMR and *GPC* measurements. The NMR spectra of poly(St-b-THF) (Run 7 in Table 2) displays signals at 1,2-1,9 ppm $CH_2CH_2(PSt)$, $CH_2(PTHF)$, 3,4 ppm $OCH_2(PTHF)$ and 6,4 - 7,2 ppm $Ph(pSt)$ Figure 1. The ratio of the integrated intensity of the peaks at 3,4 and 6,4-7,2 ppm indicates the mol ratio of *PSt/PTHF* segments to be approximately 6,9 in the block copolymer.

Table 2. Block copolymerization of polytetrahydrofuran with vinyl monomers at 70°C.

Run No	Monomer (mol.l ⁻¹)	PTHF (g/l)	Time (min)	Conversion (%)	$\bar{M}_n, 10^4$ of Block Copolymer	$R_p \cdot 10^4$ (mol.L ⁻¹ .S. ⁻¹)	PTHF Content Block Copolymer (%)
4	MMA (9,4)	50 ^a	30	5,0	28,1	2,6	8,17
5	MMA(9,4)	50 ^a	75	24,0	39,1	4,9	5,90
6	MMA(9,4)	14,2 ^a	60	3,2	27,9	0,83	8,26
7	St(8,7)	27,5 ^b	30	2,2	34,0	1,2	15,4
8	St(8,7)	27,5 ^b	75	4,5	40,6	0,88	11,3
9	EA(9,24)	27,5 ^b	30	40,0	94,7	20,6	5,0
10	AN(15)	27,5 ^b	30	2,0	-	1,57	-

^a \bar{M}_n initial PTHF = 34.000

^b \bar{M}_n initial PTHF = 66.000

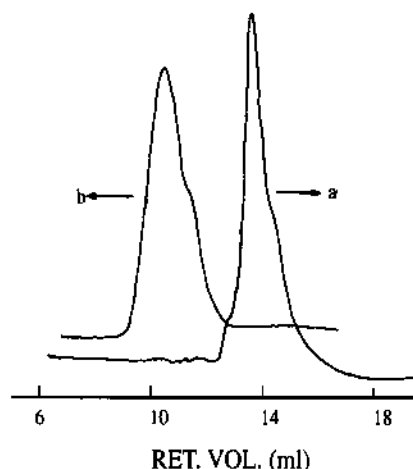


Figure 1

The agreement of this value with that obtained from G.P.C. measurements (6,4) is remarkable. G.P.C. analysis indicates also the formation of block copolymer.

Figure 2. shows the G.P.C. charts recorded with the active PTHF and block copolymer after extraction with ethanol. The new peak at higher molecular weight is ascribed to the block copolymer. IR spectrum of purified block copolymer shows a characteristic ether bond of the PTHF segments at 1100 cm⁻¹ in addition to the usual PSt bands.

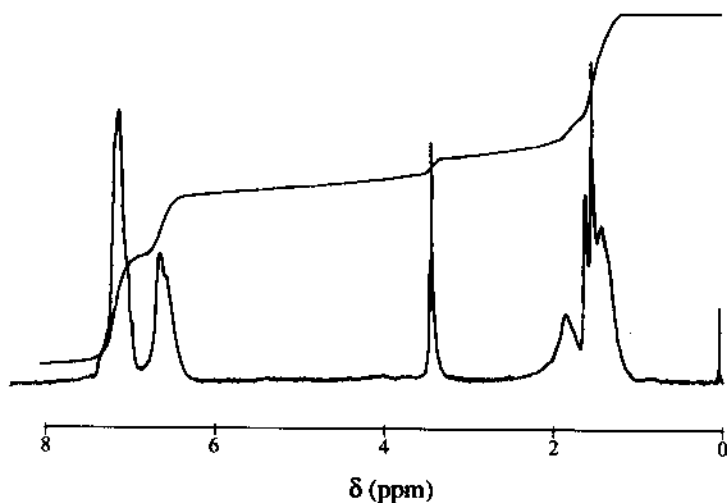


Figure 2

Similarly, $^1\text{H-NMR}$ spectrum of the block copolymer of MMA and THF possesses characteristic signals of both segments Figure 3. As can be seen from Figure 4, significant molecular weight increase due to block copolymerization was observed in this case also.

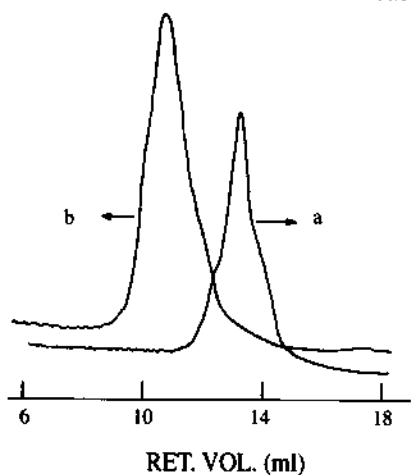


Figure 3

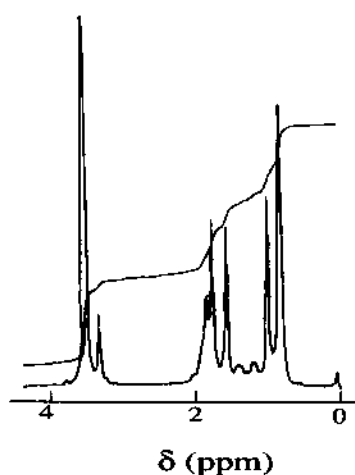


Figure 4

It should be pointed out that the termination mode of vinyl monomer used in the second stage plays an important role in the structure of the resultant block copolymers.

Notably, a block of structure ABA is obtained, if termination of macroradicals consisting of vinyl monomers occurs by combination as in the case of styrene. On the other hand block copolymers of the structure AB will be formed, if termination of macroradicals occurs by disproportionation as in the case of MMA.

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