BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 20, pp. 3955–3961, 1995
Elsevier Science Ltd
Printed in Great Britain
0032-3861/95/$10.00 + 0.00

Preparation of azo functional poly(isobutyl vinyl ether) oligomers and block copolymers via combination of living cationic and condensation polymerization

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This paper reports the synthesis and characterization of azo functional poly(isobutyl vinyl ether) oligomers and block copolymers containing poly(isobutyl vinyl ether) and oligoesterdiol segments. Isobutyl vinyl ether was polymerized using a trifluoromethanesulfonic acid/tetrahydrothiophene initiating system in dichloromethane at −30°C, and quantitatively terminated with labile azo compounds to give poly(isobutyl vinyl ether) with well-defined molecular weight and end-groups. Also, diblock copolymers with poly(isobutyl vinyl ether) and oligoesterdiol segments were synthesized by termination of living, cationically polymerized isobutyl vinyl ether with oligoesterdiol.

(Keywords: poly(isobutyl vinyl ether); labile azo groups; oligoesterdiols)

INTRODUCTION

Living cationic polymerization affords control over the molecular weight, molecular weight distribution and end-groups of the resulting polymer. Additionally, the highly reactive chain-ends of living cationic polymers can be used for the synthesis of telechelics, block copolymers and other functional polymers.

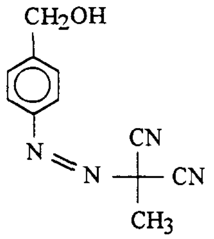
In 1984, Higashimura *et al.*[1] reported the first example of a truly living cationic polymerization of an alkyl vinyl ether initiated by an HI/I_2 system. There are now a number of initiating systems for the living cationic polymerization of alkyl vinyl ethers[2].

Recently, Webster *et al.* and Lin and Matyjaszewski[4] have reported a new initiating system for the synthesis of living alkyl vinyl ether polymers. In this system, a mixture of a strong protonic acid (trifluoromethanesulfonic acid) and a Lewis base (sulfide), which stabilizes the active chain-ends, affords the living polymerization. Goethals *et al.*[5] have used this initiating system in order to obtain macromonomers by end capping of living polymers with tertiary amines or alcohols.

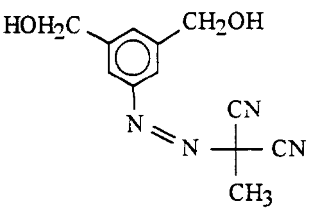
Alkyl vinyl ether block copolymers have also been prepared by other methods[2]. One method involves sequential living polymerization and is a simple way for the synthesis of block copolymers. The first monomer is polymerized to give a living polymer upon which, without quenching, the second monomer is polymerized[6–8]. Another method involves polymerization from a macroinitiator in which the functional group of the initiator is introduced into a living, cationically polymerized poly(alkyl vinyl ether)[9]. Accordingly, Nuyken *et al.*[10,11] have prepared poly(isobutyl vinyl ether) with labile azo groups available for free radical vinyl copolymerization. The method of polymer coupling has rarely been used to obtain poly(alkyl vinyl ether) block copolymers, in contrast to the frequent use of sequential living polymerization for the synthesis of living alkyl vinyl ethers. However, Rifle and coworkers[12,13] have prepared diblock copolymers containing poly(methyl methacrylate) and poly(alkyl vinyl ether) segments using a combination of living cationic and living group transfer polymerization techniques.

We now report the coupling reactions of living poly(isobutyl vinyl ether) and oligoesterdiols initiated by the trifluoromethanesulfonic acid (triflic acid)/tetrahydrothiophene system that afford ABA-type block copolymers. Furthermore, the living poly(isobutyl vinyl ether) was quenched with the hydroxy functional labile azo compounds azo I and azo II.

Azo I



Azo II



EXPERIMENTAL

Materials

Isobutyl vinyl ether (IBVE) (Aldrich) was dried overnight with calcium hydride and distilled under nitrogen. Tetrahydrothiophene (Aldrich) was dried with calcium hydride and distilled under nitrogen. Triflic acid (Aldrich, 98%) was distilled under nitrogen. Azo I and azo II were synthesized as described elsewhere[14,15]. Silica gel 60 was purchased from Merck.

Instruments

Gel permeation chromatography (g.p.c.) measurements were carried out on a Waters ALC 200 (eluent THF, narrow molecular weight polystyrene standards, refractive index detection). ^{1}H n.m.r. spectra were recorded on a Bruker AC 250 at 250 MHz.

Typical oligoesterdiol synthesis

To a Schlenk tube were added 0.698 g of 1,3-bis(hydroxymethyl)benzene **1** (5.05 mmol), 0.232 g of azo II (0.95 mmol) and 7.5 ml of pyridine. The system was purged with argon. To the reaction mixture cooled to 0–5°C, a solution of 0.73 ml of adipoyl chloride **2** (5 mmol) in 2.5 ml of THF was added dropwise. The reaction mixture was then stirred for 1.5 h at room temperature. The mixture was then poured into cold methanol and filtered. The resultant pale yellow powder was purified by dissolving in dichloromethane and reprecipitating with cold methanol (47% yield).

Table 1 Specifications of oligoesterdiol syntheses

Obtained from	M_w[a]	M_n[a]	M_n[b]	Number of azo groups per polymer chain[c]	Yield (%)
1, **2**	2420	2130	1800		69
1, azo II, **2**	3160	2830	2810	1.2	47
1, **3**	2190	1840	1750		84
1, azo II, **3**	2260	1960	1840	0.9	66

[a] From gel permeation chromatography calibrated with polystyrene standards

[b] From ^{1}H n.m.r. spectra

[c] From ^{1}H n.m.r. spectra (by assignment of the CH_3 groups of the azo functionality)

Living cationic polymerization of IBVE and end capping with azo I

Into a two-necked reaction flask were injected 4.4 ml of freshly distilled dichloromethane, 1.3 ml of IBVE (10 mmol) and 220 μl of tetrahydrothiophene with stirring under an argon atmosphere. A rubber septum was placed in the open neck of the flask and the argon inlet was closed. The solution was cooled to −30°C with a CO_2/acetone mixture. Then, 22 μl of triflic acid (0.25 mmol) was syringed into the system with stirring. The reaction was allowed to continue for 30 min. Then a solution of 0.268 g of azo I (1.25 mmol) in 4.4 ml of dichloromethane was prepared and syringed into the reaction mixture followed by 60 μl of 2,6-lutidine. The cooling bath was removed and the system was allowed to warm up to room temperature. Stirring was continued for 1 h, then the solution was placed in a separating funnel and twice extracted with water to remove excess azo I and the salt of 2,6-lutidine. The organic phase was dried with Na_2SO_4 and evaporated *in vacuo* to give 1.05 g of poly(IBVE) end capped with azo I.

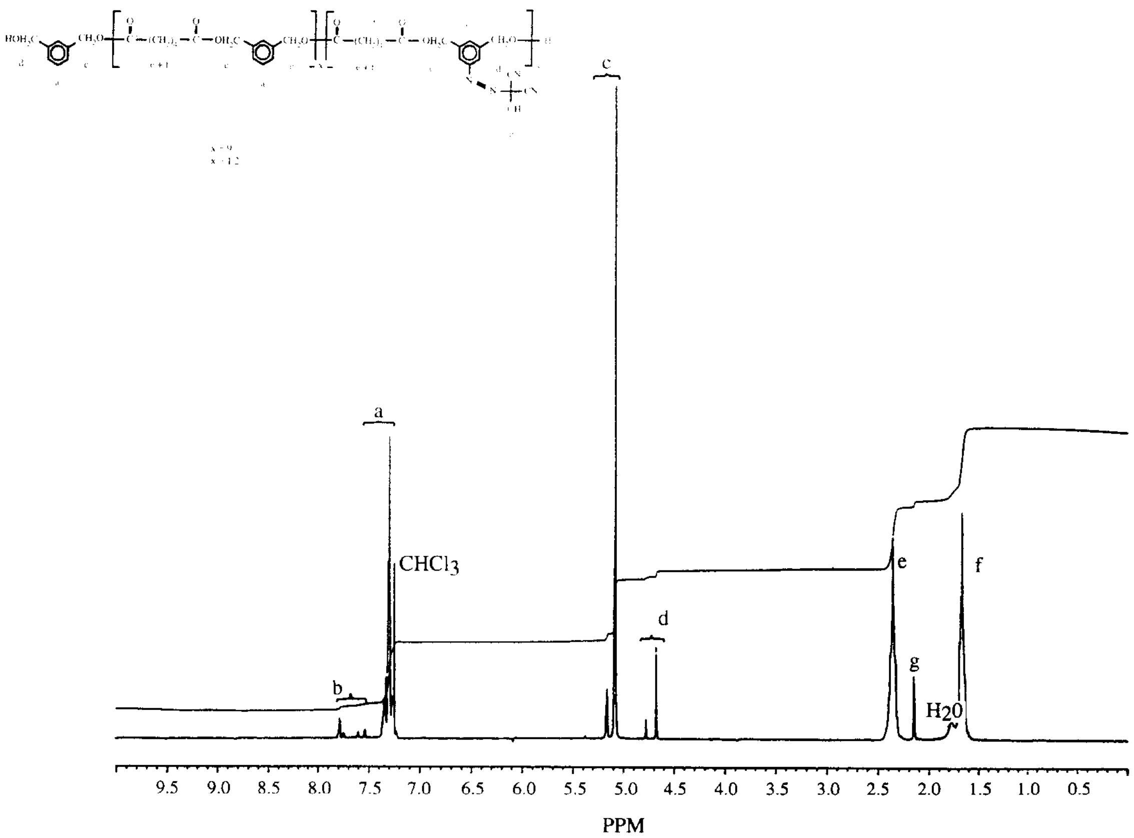


Figure 1 ^{1}H n.m.r. spectrum of oligoesterdiol **1**/azo II/**2** in $CDCl_3$

Polymer-coupling reaction with oligoesterdiol 1/azo II/2

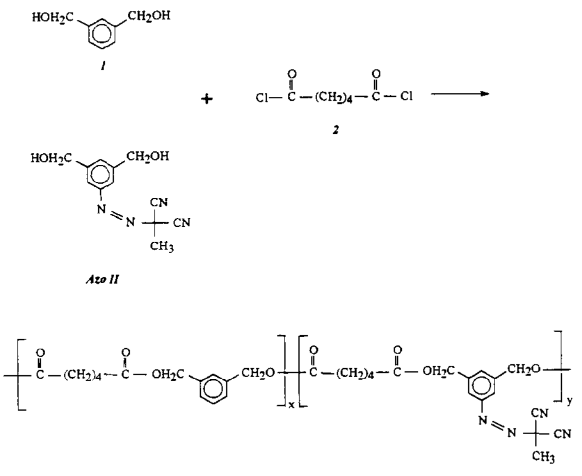
IBVE was first polymerized in a similar manner to that described above. To the reaction mixture under argon were added 0.395 g of oligoesterdiol **1**/azo **II**/**2** in 4.4 ml of dichloromethane and 60 μl of 2,6-lutidine. The cooling bath was removed and the mixture was allowed to warm up to room temperature. Stirring was continued for 2.5 h, then the solution was transferred to a separating funnel and twice extracted with water. The organic phase was dried over Na_2SO_4, filtered and evaporated *in vacuo* to give 1.39 g of the block copolymer.

RESULTS AND DISCUSSION

Synthesis of oligoesterdiols

1,3-Bis(hydroxymethyl)benzene **1** itself, or in a mixture with 3,5-bis(hydroxymethyl)phenylazomethylmalononitrile (azo II), was reacted with adipoyl chloride **2** or terephthaloyl chloride **3** a non-stoichiometric molar ratio of diol to acid chloride. An overview of the results is given in *Table 1*.

A typical esterification reaction scheme is as follows.



As can be seen from *Table 1*, the M_n values obtained from ^{1}H n.m.r. (*Figure 1*) are in good agreement with those obtained from g.p.c. G.p.c. chromatograms of the oligoesterdiols show typical oligomeric distributions (*Figure 2*). The peaks can be related to the number of repeat units.

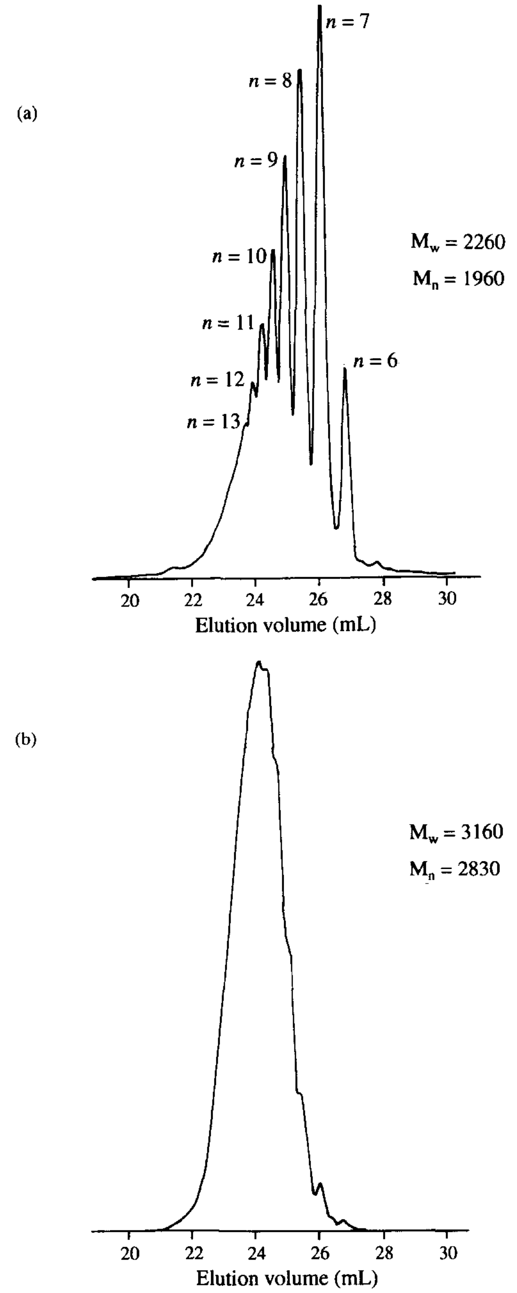


Figure 2 G.p.c. chromatograms (THF as eluent) of oligoesterdiols: (a) **1**/azo II/**3**; (b) **1**/azo II/**2**

Table 2. Conditions and results for the living cationic polymerization of IBVE

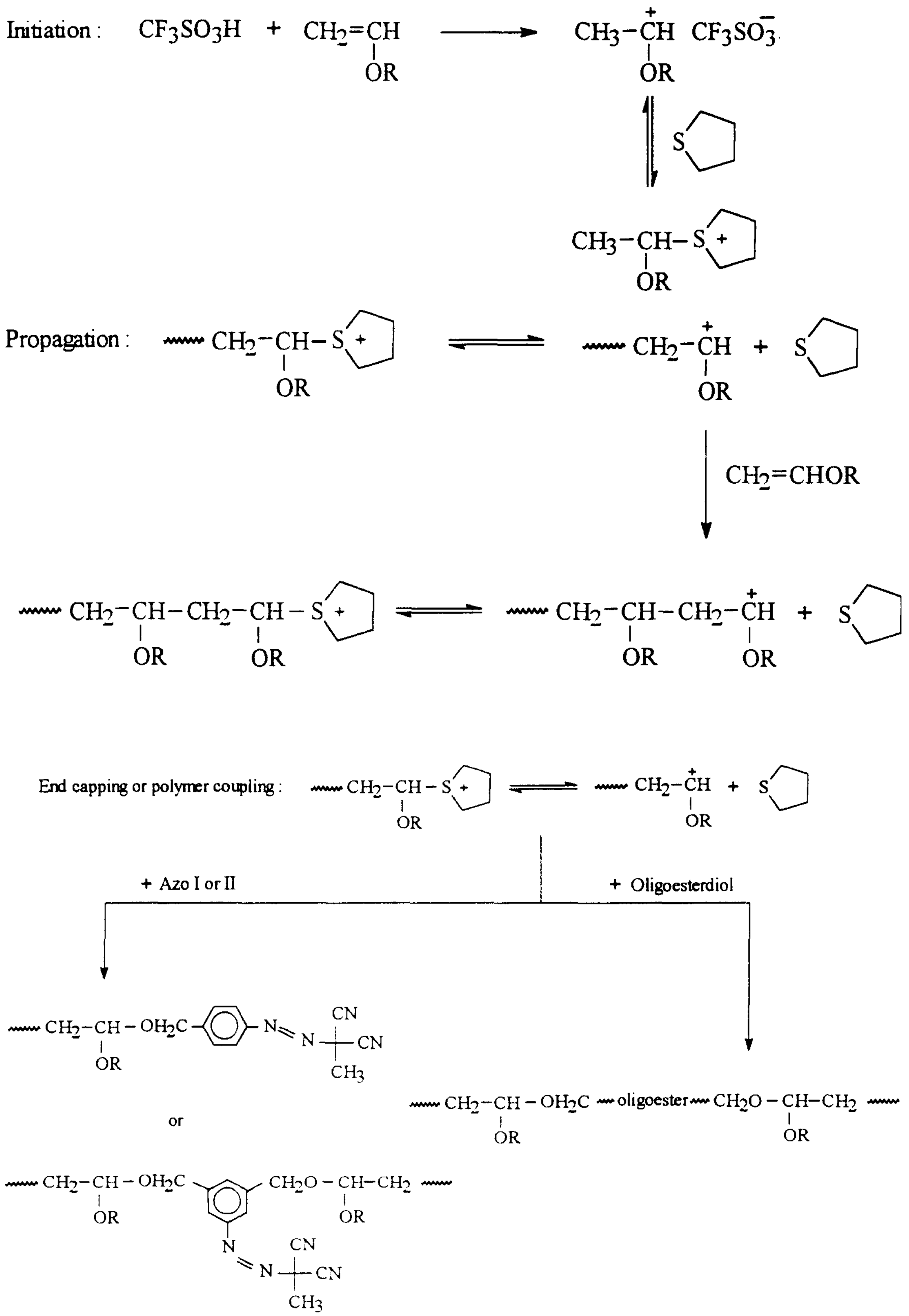
$[\text{IBVE acid}]_0/[\text{triflic acid}]_0$	End-capping compound	$M_{n,calc}$ [a]	$M_{n,exp}$ [b]	$M_{n,n.m.r.}$	M_w/M_n [b]
10/0.20	Azo I	5220	5420	5330	1.05
10/0.25	Azo II	8260	8870		1.23

[a] $M_{n,calc} = ([\text{IBVE}]_0/[\text{triflic acid}]_0)M_{monomer} + M_{\text{end-capping compound}}$

[b] M_n and M_w obtained from g.p.c. calibrated with polystyrene standards

Living cationic polymerization of IBVE

IBVE was polymerized using a triflic acid/tetrahydrothiophene initiating system in dichloromethane at −30°C. At the end of a given reaction time, azo I, azo II or an oligoesterdiol was introduced into the reaction mixture followed by 2,6-lutidine as a proton scavenger. The reaction scheme is as follows.



R = isobutyl group

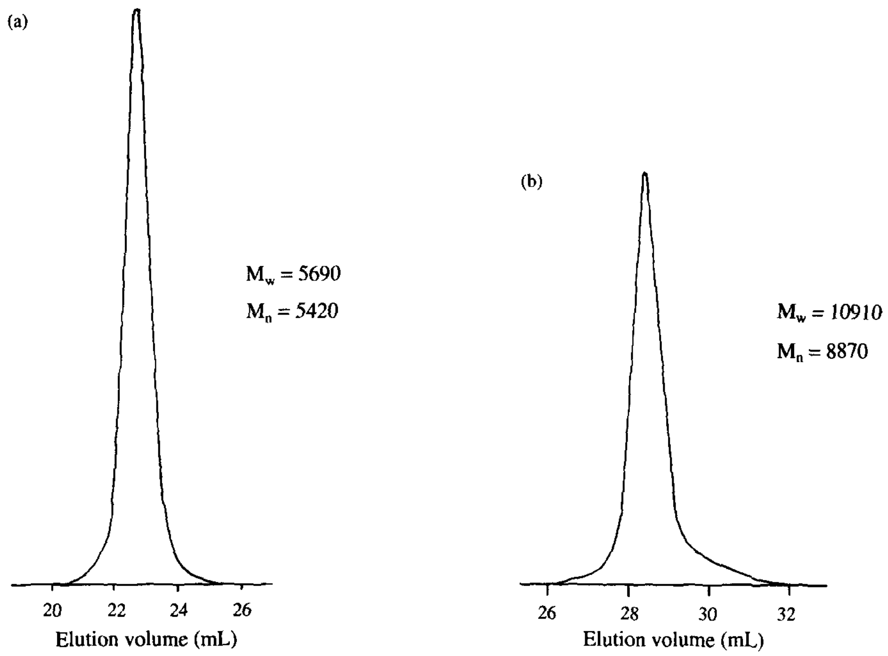


Figure 3 G.p.c. chromatograms (THF as eluent) of poly(IBVE) terminated with (a) azo I and (b) azo II

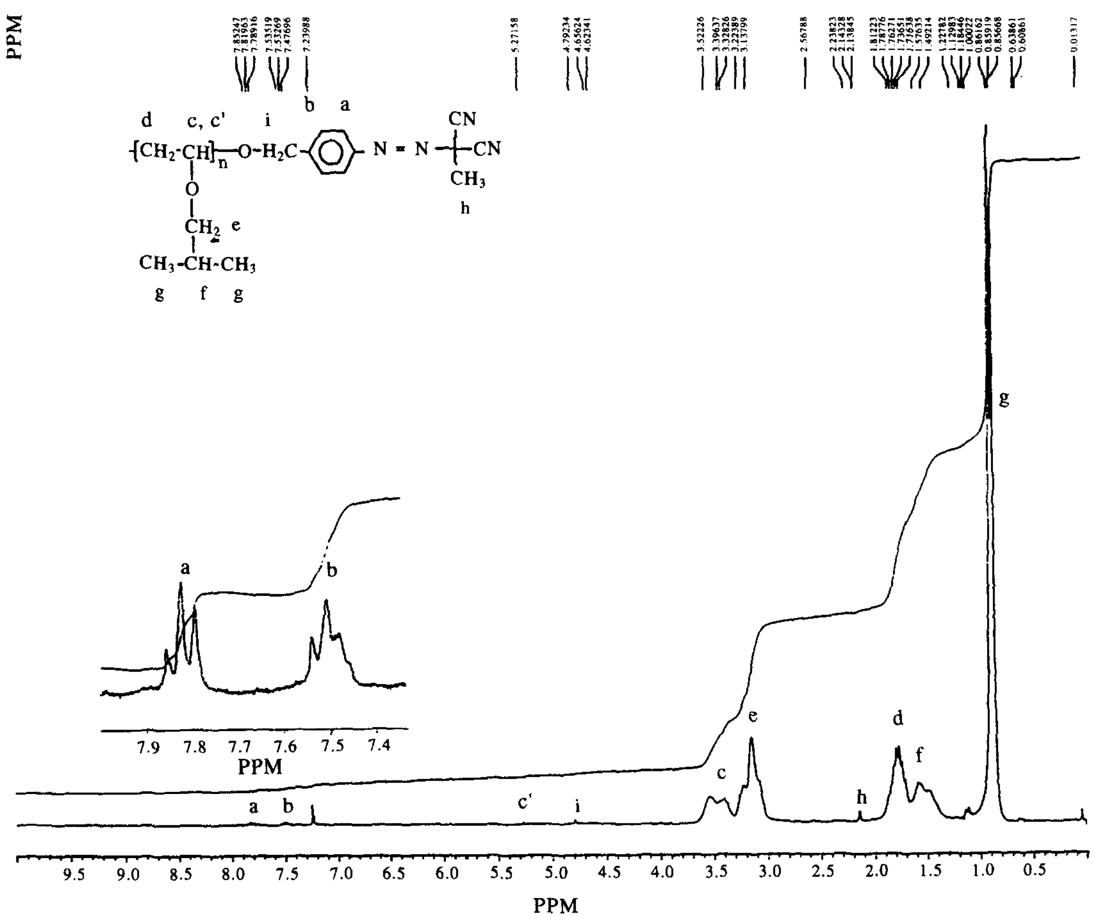


Figure 4 ^{1}H n.m.r. spectrum of azo I terminated poly(IBVE) in $CDCl_3$

After termination the polymer was quantitatively isolated from the reaction mixture. An overview of the results is given in *Table 2*.

Figure 3 shows the g.p.c. chromatograms of poly(IBVE) end capped with azo I and azo II. Azo I terminated poly(IBVE) is characterized by a peak at 5.3 ppm from the acetal proton in the ^{1}H n.m.r. spectrum (*Figure 4*).

The reaction mixture obtained from oligoesterdiol **1**/azo II/**2** coupled with poly(IBVE) was analysed by g.p.c.

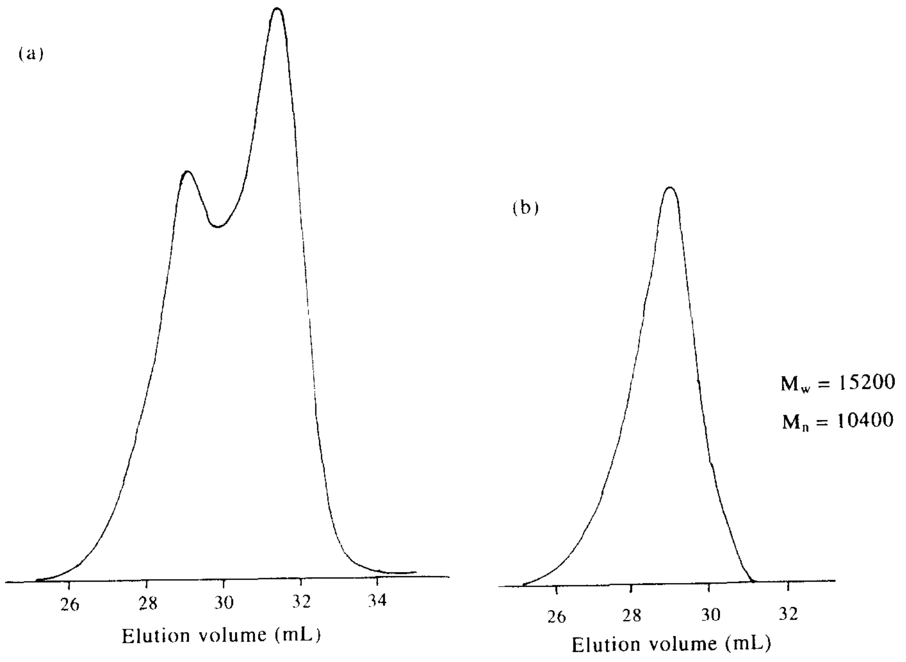


Figure 5 G.p.c. chromatograms (THF as eluent): (a) reaction mixture containing block copolymer and oligoesterdiol; (b) block copolymer

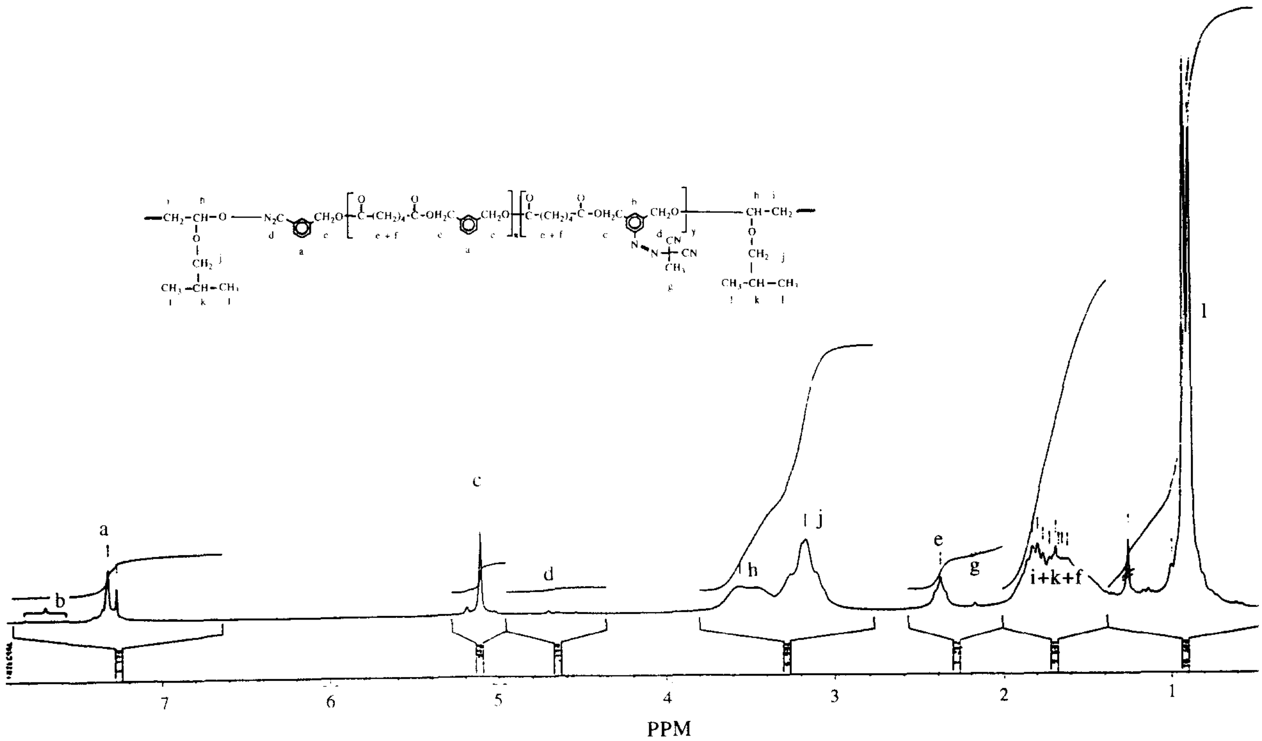


Figure 6 ^{1}H n.m.r. spectrum of the block copolymer in CDCl$_3$

(*Figure 5a*). The chromatogram for the block copolymerization reaction shows a bimodal peak, of which the lower molecular weight fraction can be attributed to unreacted oligoesterdiol and the higher molecular weight fraction to the block copolymer. This reaction mixture was separated by column chromatography (silica gel 60, ethyl acetate/ethanol (9/1 v/v) as eluent). The resultant solution was evaporated to give the block copolymer in high yield. G.p.c. analysis of the block copolymer shows a single peak at high molecular weight (*Figure 5b*). The formation of the block copolymer was also established by ^{1}H n.m.r. (*Figure 6*). Both g.p.c. and ^{1}H n.m.r. clearly show the presence of both poly(IBVE) and oligoesterdiol segments corresponding to the theoretical composition. According to the ^{1}H n.m.r. integrations of the peaks at 3.1–3.5 ppm for poly(IBVE) and the peak at 2.4 ppm for the oligoesterdiol, the molar ratio of poly(IBVE) to oligoesterdiol segments in the block copolymer was 2.1.

CONCLUSION

We prepared labile azo group containing poly(IBVE)s using a living cationic polymerization method. Such polymers may be useful as macroinitiators in vinyl polymerization. Furthermore, novel block copolymers containing poly(IBVE) and oligoesterdiol segments were prepared by coupling of living poly(IBVE) with oligoesterdiols. Soft segments were thus connected to hard segments resulting in ABA-type block copolymers.

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