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Synthesis of block copolymers by combination of cationic and initer polymerization system

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Trityl terminated poly(butyl vinyl ether) was obtained by the polymerization of butyl vinyl ether with triphenylcarbonium tetrafluoroborate–thiolane initiator system. In this system, thiolane was used to prevent both hydride abstraction of trityl cation and chain transfer of growing chain of butyl vinyl ether cation. Trityl terminated polymers served as thermal *initer* for the polymerization of methyl methacrylate which proceeded via a quasi-living radical mechanism. This procedure makes it possible to prepare block copolymers. © 1997 Elsevier Science Ltd.

(Keywords: functional polymer; initer; block copolymer)

INTRODUCTION

There have been several classical methods for the preparation of block copolymers, which generally involve the successive polymerization of two or more monomers by the same mechanism. Transformation reactions extend the range of possible monomer combinations in block copolymer[1,2]. This approach allows polymers produced by one type of polymerization to be terminally functionalized by groups capable of initiating a different mode of polymerization. The synthesis of block copolymers may be achieved by cationic and radical[3–5], anionic and radical[6–9], condensation and radical[10–13], redox and thermal radical[14,15], and thermal radical and photochemical radical polymerization[16–19] routes.

The iniferter method, for the preparation of block copolymers, has been extensively explored during the last decade, primarily by Otsu *et al.*[20]. In this concept, *iniferter* (initiator-transfer agent-terminator) was used to design the structure of polymer chain ends in radical polymerization[21]. Several organic disulfides and phenylazotriphenyl methane were found to serve as photo and thermal iniferters[20–23], respectively. Polymers, obtained by using iniferters, still have iniferter function capable of initiating the polymerization of another monomer yielding block copolymers.

It has been shown[24,25] that radical transfer polymerization can be used for the preparation of polymers with functional end groups. Recently, we have reported[26] that trityl terminated polymers were synthesized by using chain transfer compound triphenyl methyl mercaptan. These polymers were shown to be capable of acting as thermal *initer* (initiator-terminator).

On the basis of these approaches, the present work deals with the possibility of synthesis of polymer with terminal trityl group, using corresponding cationic initiator, and its further use for the preparation of block copolymer.

As it will be shown below, polymerization of butyl vinyl ether was carried out with a combination of triphenyl carbonium tetrafluoroborate–thiolane initiator system. Thiolane was used to prevent both hydride abstraction of trityl cation and chain transfer reactions dominating vinyl ether polymerization[27]. Trityl terminated poly(butyl vinyl ether)[28] was subsequently used to initiate free radical polymerization of methyl methacrylate via initer mechanism[26,29].

EXPERIMENTAL

Triphenylcarbonium (trityl) tetrafluoroborate ($Tr^+BF_4^-$, Aldrich, USA) and thiolane (tetrahydrothiophene, THT, Aldrich) were used as received. Butyl vinyl ether (BVE, Fluka), methyl methacrylate (MMA, Petkim, Turkey) and solvents (Fluka, Switzerland) were purified by conventional drying and distillation procedures.

The ^{1}H n.m.r. spectra were taken on a Bruker (model 200) in $CHCl_3$ solution with tetramethylsilane as internal standard. U.v. spectra were taken by using Perkin–Elmer (model Lambda 2) spectrophotometer in CH_2Cl_2 solution. G.p.c. analyses were performed with a set-up consisting of a Waters pump (model 600 E) and Ultrastyragel columns with porosities 500 and 10 Å, respectively. THF was used as eluent at a flow rate of 1 ml min^{-1} and detections were carried out with Waters Differential Refractometer (model 410) and Photodiode Array Dedector (model 996). Samples were injected by using 20 μl sample loop. Concentrations were normally in the range of 2–3% w/v. Molecular weights were calculated with the aid of polystyrene standards.

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Table 1 Trityl terminated poly(butyl vinyl ether) polymerization of butyl vinyl ether by using $Tr^+BF_4^-$ in the presence of THT[a]

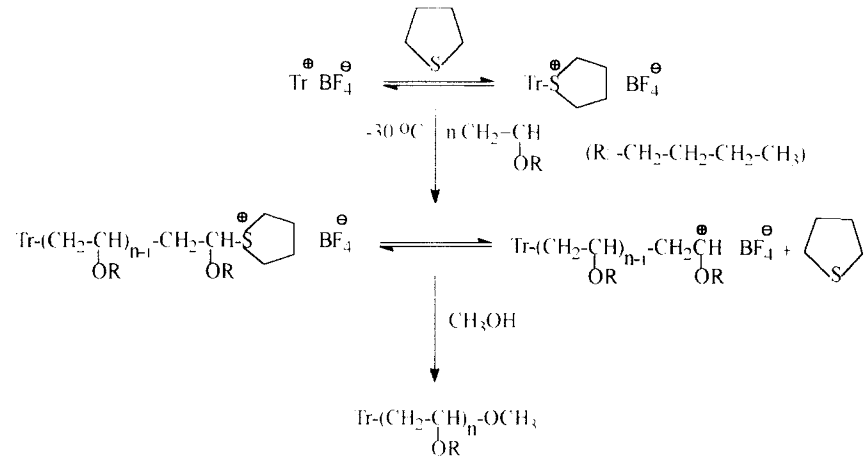
Run	Time h	Conversion %	Molecular weight Calculated[b]	U.v.[c]	N.m.r.	G.p.c.[d]	M_w/M_n
1	0.5	77.2	7720	8330	8860	7000	1.18
2	1.0	93.2	9320	9280	10 300	10 100	1.21

[a] $[Tr^+BF_4^-] = 0.02\,mol\,l^{-1}$, $[BVE] = 2\,mol\,l^{-1}$, $[THT] = 2\,mol\,l^{-1}$, $-30^\circ C$

[b] $M_{calc} = ([BVE]/[Tr^+BF_4^-])$. Conversion %. M_{BVE}

[c] $\epsilon_{262\,nm} = 1305\,mol^{-1}\,l\,cm^{-1}$

[d] Standard polymer: polystyrene, eluent: THF, $1\,ml\,min^{-1}$



Tr-PBVE

Preparation of trityl terminated polymers (Tr-PBVE)

BVE ($2\,mol\,l^{-1}$) and THT ($2\,mol\,l^{-1}$) as monomer and carbocation stabilizer, respectively, in dichloromethane (CH_2Cl_2) were put into polymerization tubes. The mixtures were outgassed in the usual manner and placed in a constant temperature bath at $-30^\circ C$. After that, $Tr^+BF_4^-$ ($0.02\,mol\,l^{-1}$) as cationic initiator was added to polymerization tubes. At the end of the reaction, the mixtures were poured into a ten-fold excess of methanol containing some amount of base. After decantation of solvents and drying of residuals, trityl terminated poly(butyl vinyl ether)s (Tr-PBVE) were obtained.

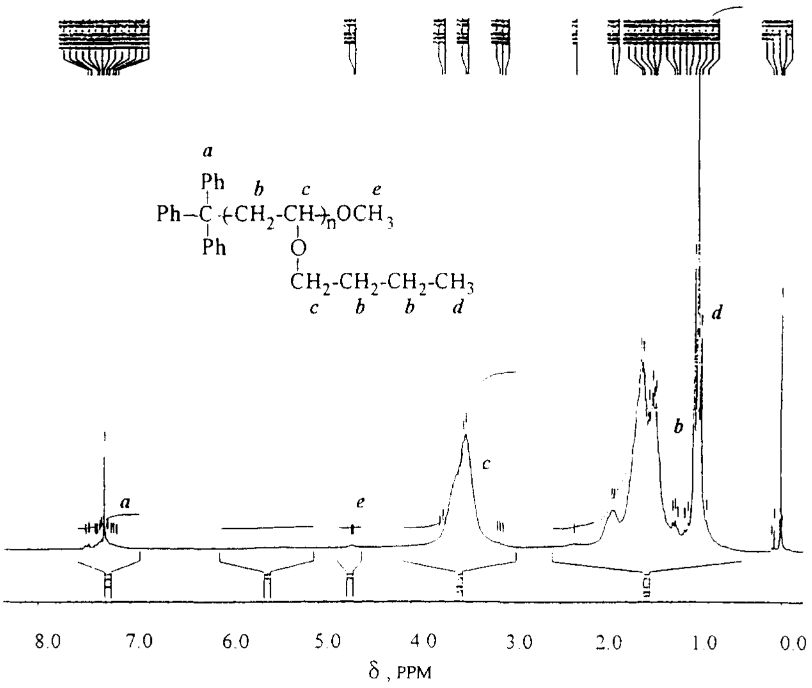


Figure 1 ^1H n.m.r. spectrum of Tr-PBVE

Table 2 Polymerization of MMA initiated by Tr-PBVE in toluene[a]

Run	Time h	Temp. °C	[MMA] $\mathrm{mol\,l^{-1}}$	Conv. %	M_n[b]	ΔM_n[b]	Fractions extracted PBVE[c] %	 Block[d] %
1	7	80	4.72	0.66	12 800	2700	79.3	20.7
2	14	80	4.72	18.90	27 800	17 700	18.7	81.3
3	21	80	4.72	20.30	32 100	22 000	15.6	84.4
4	30	80	4.72	38.10	46 400	36 300	9.0	91.0
5	41	80	4.72	84.40	77 200	67 100	2.4	97.6
6	30	90	4.72	56.10	48 200	38 100	8.8	91.2
7	30	90	2.36	59.40	64 400	54 300	6.1	93.9

[a] [Tr-PBVE] = $50\,\mathrm{g\,l^{-1}}$ (M_n = 10 100)

[b] Measured in g.p.c. Standard polymer: polystyrene, eluent: THF, $1\,\mathrm{ml\,min^{-1}}$

[c] Soluble part in CCl_4

[d] Insoluble part in CCl_4

Deactivation of trityl terminated polymers (DPPH-PBVE)

Tr-PBVE ($0.012\,\mathrm{mol\,l^{-1}}$) and 2,2-diphenyl-1-picrylhydrazyl (DPPH, $0.06\,\mathrm{mol\,l^{-1}}$) in toluene were degassed and heated at 100°C for 2 h. At the end of the reaction, the mixtures were poured into ten-fold excess of methanol. After decantation of solvents and drying of residuals, deactivated polymers (DPPH terminated polymers, DPPH-PBVE) were obtained.

Block copolymerization

MMA (4.72 or $2.36\,\mathrm{mol\,l^{-1}}$) and Tr-PBVE ($50\,\mathrm{g\,l^{-1}}$) mixtures in toluene were put into polymerization tubes, degassed and heated at 80 or 90°C. After polymerization for a given time, the contents of the tubes were poured into methanol and precipitated polymers were filtered and dried. The separation of the block copolymers was carried out by extracting with appropriate solvents.

Control experiments with DPPH-PBVE were performed under the same conditions.

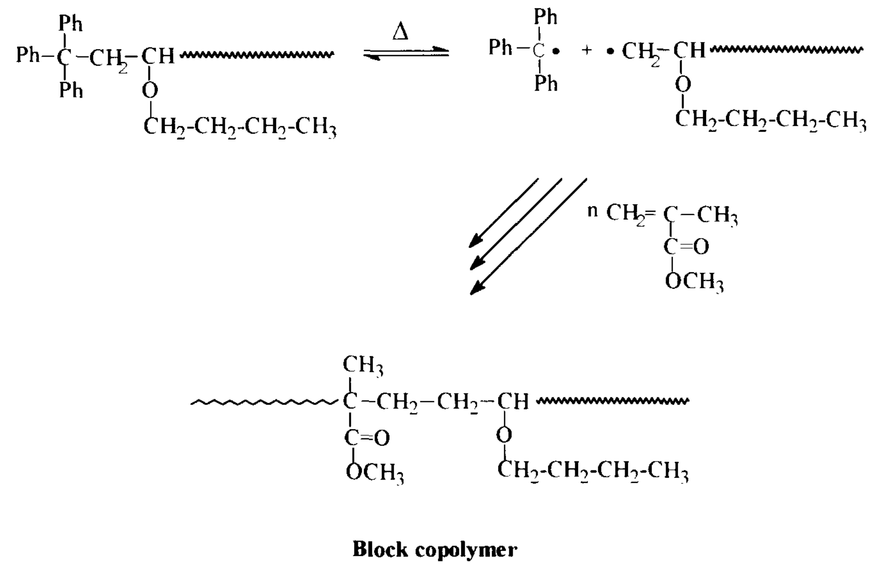
RESULTS AND DISCUSSION

BVE was polymerized in the presence of $Tr^+\ BF_4^-$ and thiolane in order to obtain polymers with trityl end groups (*Table 1*).

The introduction of trityl groups into PBVE was evidenced by ^{1}H n.m.r. As can be seen from *Figure 1*, aromatic protons appear in the 7.2 ppm region, in addition to peaks at 3.5 ppm for C$\underline{H}$–O and O–C$\underline{H}_2$ and 0.9–1.9 ppm for C$\underline{H}_2$–CH–O and alkyl protons, respectively. The u.v. spectrum of the polymer possesses an absorption band at around the 262 nm region, indicating attachment of trityl end groups. In addition, g.p.c. analysis shows no contamination by physically entrained $Tr^+BF_4^-$ in the polymers.

Radical polymerization with polymeric thermal initer

The polymer obtained has a trityl moiety at one end. Tr-PBVE was used as a thermal initer in the polymerization of MMA (*Table 2*), according to the following reactions



The plot of molecular weight change of the polymers ($\Delta M_n = M_{n,i} - M_{n,0}$) against the conversion of MMA is shown in *Figure 2*. Here, $M_{n,i}$ and $M_{n,0}$ denote molecular weight of the polymer recorded after various polymerization times and of the prepolymer (Tr-PBVE), respectively. As can be seen, ΔM_n of the polymers

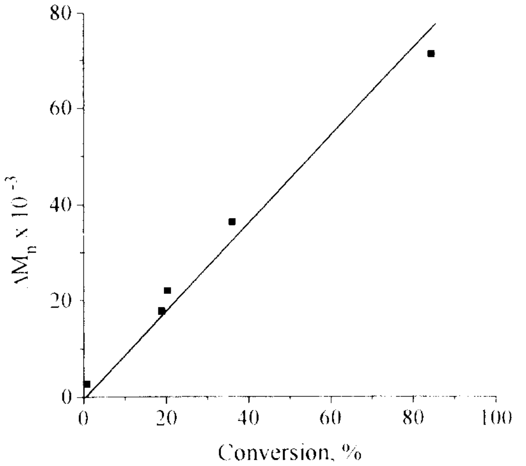


Figure 2 Polymerization of MMA with Tr-PBVE in toluene at 80°C. $\Delta M_n = M_{n,i} - M_{n,0}$ [MMA] = 4.72 mol l^{-1}, [Tr-PBVE] = 50 g l^{-1} (M_n = 10 100)

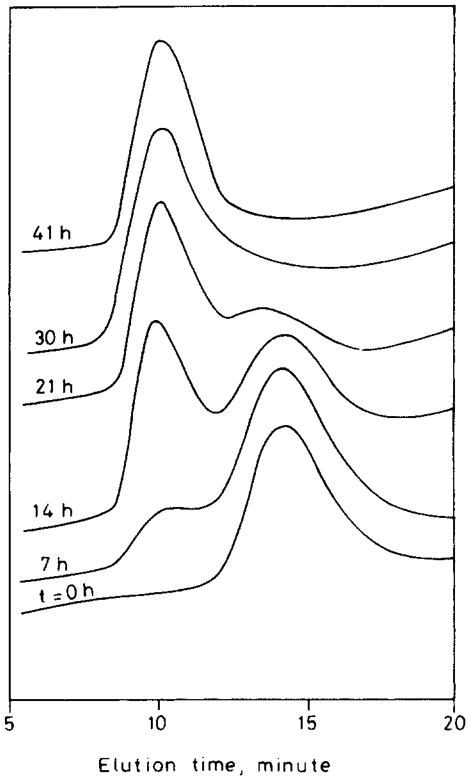
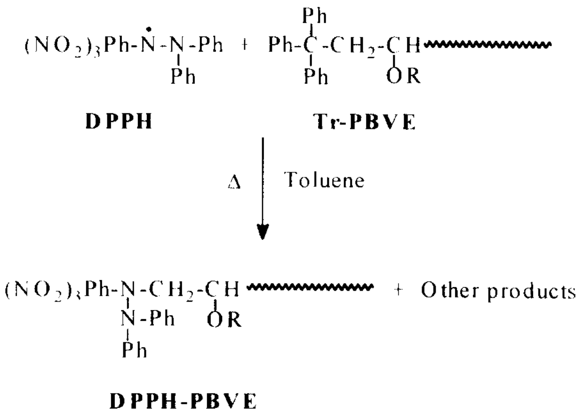


Figure 3 G.p.c. traces for MMA polymerized with Tr-PBVE in toluene (80°C) at each time. Standard polymer: polystyrene. Eluent: THF, 1 ml min^{-1}

increased linearly with conversion, which indicates that this polymerization proceeds via a quasi-living radical mechanism in a manner proposed by Otsu *et al.*[20]. *Figure 3* shows the g.p.c. traces of copolymerization of MMA with Tr-PBVE at various reaction times. The initial Tr-PBVE g.p.c. trace showed a unimodal molecular weight distribution and then when MMA was polymerized in the presence of Tr-PBVE a new peak at higher molecular weight also appeared in the g.p.c. trace, which itself shifted to the higher molecular weight with time. Block copolymers were purified by extracting in carbon tetrachloride where poly(butyl vinyl ether) homopolymer is soluble. Residual traces of poly(methyl methacrylate) homopolymer could still be present but were not detectable by g.p.c. and n.m.r.

In order to check the initiation capability of trityl end groups we have performed deactivation and polymerization experiments. For this purpose trityl terminated polymer was heated in toluene in the presence of diphenylpicrylhydrazyl (DPPH). The resulting polymer is expected to have DPPH end groups according to the reaction



Moreover, this polymer was proved to have no initiating functionality. Indeed, polymerization of MMA using DPPH terminated polymer (DPPH-PBVE) failed to produce any block copolymer but only homo PBVE under similar experimental conditions described for trityl terminated polymer. The absorption band of the trityl terminated polymer disappeared upon treatment with DPPH at 100°C in toluene. This behaviour explains not only the presence of trityl end groups but also dissociation of these groups by thermolysis.

In conclusion, these results indicate that the combination of cationic polymerization and the initer technique can be applied to produce a block copolymer.

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