

<sup>a</sup> Istanbul Technical University, Faculty of Sciences, Department of Chemistry,  
Y. Levent, Istanbul, Turkey

<sup>b</sup> University of Yildiz, Department of Chemistry, Sisli, Istanbul, Turkey

## **Polymerization of n-Butyl Vinylether Initiated by Polymeric Peroxycarbamates and Active Polystyrenes**

Yusuf Yagci<sup>a\*</sup>, Metin Acar<sup>a</sup>, Gurkan Hiza<sup>b</sup>, Huseyin Yildirim<sup>b</sup>,  
and Bahattin Baysal<sup>a</sup>

(Received 12 February 1987)

### **SUMMARY:**

The free radical promoted cationic polymerization of n-butyl vinylether (BVE) was achieved by thermal decomposition of polymeric peroxycarbamates (PPC) or active polystyrene (APS), having fragments of PPC in the presence of diphenyliodonium hexafluorophosphate ( $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ ) or silver tetrafluoroborate ( $\text{AgBF}_4$ ). Polymerizations were accompanied by phase separation. Formation of block copolymers, mainly in the solid phase, was evidenced by NMR spectroscopy. Polymer samples obtained by this procedure contained only a very small fraction of block copolymer structure due to the phase separation and very effective chain transfer reactions predominating the cationic polymerization of BVE.

### **ZUSAMMENFASSUNG:**

Durch die thermische Zersetzung von polymeren Peroxycarbamaten (PPC) oder von mit Anteilen von PPC aktivierten Polystyrolen (APS) wurde in Gegenwart von Diphenyliodoniumhexafluorophosphat ( $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ ) oder von Silbertetrafluoroborat ( $\text{AgBF}_4$ ) die durch freie Radikale promovierte kationische Polymerisation von n-Butylvinyläther (BVE) erreicht. Während der Polymerisation wurde eine Phasenseparation beobachtet. Die im wesentlichen in der festen Phase gebildeten Blockcopolymeren wurden mittels NMR-Spektroskopie nachgewiesen. Die so gewonnenen Polymerproben enthielten infolge dieser Phasenseparation und der bei der kationischen Polymerisation des BVE dominierenden Kettentransferreaktion nur sehr kleine Anteile an Blockcopolymeren.

\* Correspondence author.

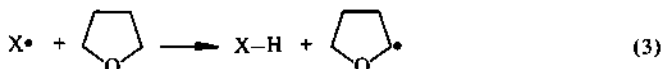
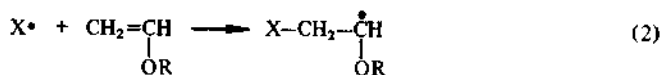
### Introduction

The use of an active polymer with one or more labile groups as a macromolecular initiator for the polymerization of a second monomer provides the possibility of a relatively simple method for the preparation of block copolymers having controlled structure. Recently, synthetic conditions and characteristics of active polymers with peroxy, azo, and azoperoxy groups and of the corresponding block copolymers have been extensively reviewed by Simionescu et al.<sup>1</sup> Of particular interest are several types of polymeric peroxy-carbamates (PPC) which contain an extensive number of peroxy bonds. They have been synthesized and utilised<sup>2-5</sup> to prepare block copolymers by two step procedures. This technique is indeed efficient, but applicability is limited to free radical susceptible monomers. On the other hand it is of great desire to synthesize block copolymers from monomers polymerizable by different mechanisms. We have recently reported<sup>6-8</sup> a new procedure to synthesize block copolymers via cationic and free radical routes.

It was shown<sup>9-11</sup> that oxidation of electron donor radicals to the corresponding carbocations induces cationic polymerization of cyclic ethers and alkyl vinyl ethers. The overall process may be represented as follows:



Useful oxidants include diaryliodonium<sup>10</sup> and silver(I) salts<sup>11</sup>. For alkyl vinyl ethers electron donor free radicals are obtained by radical addition to the monomer, whilst for cyclic ethers, such as tetrahydrofuran (THF), they are obtained by hydrogen abstraction. In the former case subsequent oxidation of alkoxyalkyl radicals will ensue initiation of cationic polymerization and the initial radicals will be incorporated into the resultant polymer.



In this work PPCs and active polystyrenes (APS) were used as free radical sources in conjunction with an iodonium or silver salt in the promoted cationic polymerization of *n*-butyl vinyl ether (BVE). Using APS this procedure enables block copolymers of BVE to be produced, since the free radical source possesses polystyrene segments.

Experimental

Materials

Bis(4-isocyanatocyclohexyl)methane (H-MDI), a product of Du Pont de Nemours and Co., was distilled under reduced pressure before use. 2,5-Dimethyl-2,5-dihydroperoxy hexane (Luperox 2,5-2,5), a product of Lucidol Division Pentwalt Corp, was recrystallised twice from tetrachloromethane (CCl<sub>4</sub>). Peroxy content was 99% of the theoretical value. Dibutyltin dilaurate (T-12), a product of Cincinnati Milacron Chemical Inc., 2,2,4-trimethyl-hexamethylene diisocyanate (T-MDI), a product of Yeb-Chemie AG, and AgBF<sub>4</sub> (Fluka) were used as purchased. Diphenyliodonium hexafluorophosphate was synthesized according to the published method<sup>12</sup>.

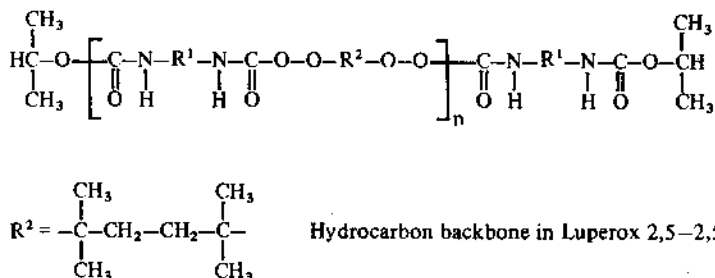
Styrene, BVE, and solvents were purified by conventional drying and distillation procedures.

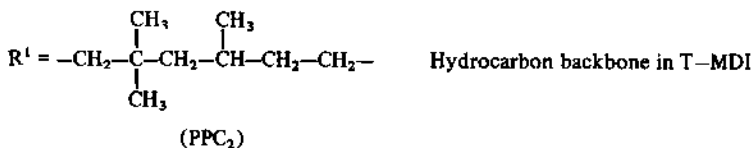
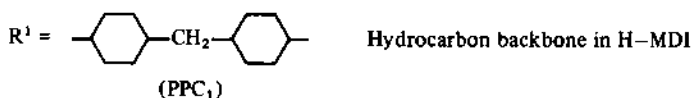
Analysis

Isocyanate analyses and peroxygen contents of PPSs and APSs were performed as described previously<sup>3</sup>. The NMR spectra were taken on a Varian EM 390 in CCl<sub>4</sub> solution with tetramethylsilane as internal standard. GPC chromatograms were obtained using a Knauer M64 instrument. Molecular weights were calculated according to polystyrene standards.

Preparation of PPCs

Two types of PPC were prepared by reacting equimolar amounts of the corresponding diisocyanate with the hydroperoxide (Luperox 2,5-2,5) in the presence of T-12. Synthetic details were described elsewhere<sup>4,5</sup>. The chemical structure of PPC can be represented as follows:





PPC<sub>1</sub>: Molecular weight: 1150; peroxygen content: 10.2.

PPC<sub>2</sub>: Molecular weight: 940; peroxygen content: 10.7.

### Preparation of APS

Solutions of styrene containing PPC were degassed and sealed in the usual manner. They were then heated in a thermostated bath at 80°C for given times. The active polymer was precipitated with tenfold methanol, filtered, and dried.

### Polymerization of BVE

Solutions of BVE containing given amounts of PPC or APS and Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup> or AgBF<sub>4</sub> were degassed and placed in a bath thermostated at 80°C for the required time. At the end of this time tacky polymers were precipitated into methanol containing a small amount of base.

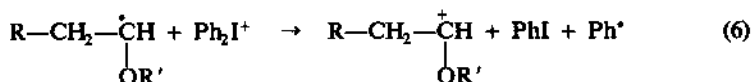
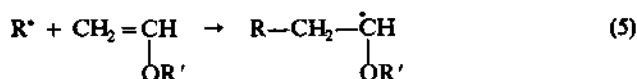
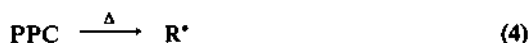
### Results and Discussion

The results of the BVE polymerization initiated by PPCs are given in Tab. 1, which shows that in the presence of the oxidant salts the cationic polymerization of BVE can be initiated readily by the thermal decomposition of PPCs. Conversions to PBVE are higher in the presence of the iodonium salt than of the silver salt. This can be explained on the basis of the generation of phenyl radicals by diphenyl ions reacting with alkoxyalkyl radicals according to reaction (6).

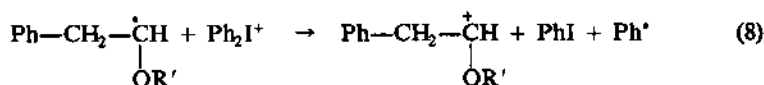
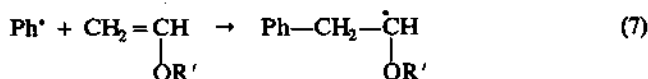
*Polymerization of n-Butyl Vinylether*

Tab. 1. Cationic polymerization of n-butyl vinylether at 80 °C. (In all cases 20% (v/v) CH<sub>2</sub>Cl<sub>2</sub> were used in order to facilitate the dissolution of the salts).

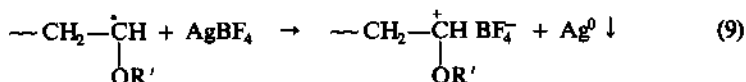
PPC (M)	Salt (M)	Heating time (min)	Conversion (%)
PPC <sub>1</sub> (1.2 · 10 <sup>-2</sup> )	Ph <sub>2</sub> I <sup>+</sup> PF <sub>6</sub> <sup>-</sup> (8 · 10 <sup>-2</sup> )	25	79
PPC <sub>1</sub> (1.2 · 10 <sup>-2</sup> )	AgBF <sub>4</sub> (8 · 10 <sup>-2</sup> )	420	56
PPC <sub>2</sub> (2 · 10 <sup>-2</sup> )	Ph <sub>2</sub> I <sup>+</sup> PF <sub>6</sub> <sup>-</sup> (8 · 10 <sup>-2</sup> )	30	60
PPC <sub>2</sub> (2 · 10 <sup>-2</sup> )	AgBF <sub>4</sub> (4 · 10 <sup>-2</sup> )	150	50



Phenyl radicals are capable of reacting with BVE thus generating radicals which can be oxidized by diphenyliodonium ions. In this way the initiation of growing (cationic) chains is multiplied.



AgBF<sub>4</sub> acts as a one electron oxidant in a manner similar to the iodonium salt. In this case polymerizations are accompanied by the formation of metallic silver either as a black precipitate or in the colloidal form.



Tab. 2. Free radical polymerization<sup>a</sup> of styrene initiated by PPC<sub>1</sub> at 80°C.

PPC <sub>1</sub> (M)	Heating time (min)	Conversion (%)	Peroxygen content (%)	APS
$3.2 \cdot 10^{-2}$	60	13.6	1.89	APS <sub>1</sub>
$6.4 \cdot 10^{-2}$	60	38.3	—	APS <sub>2</sub>
$12.8 \cdot 10^{-2}$	60	35.2	0.98	APS <sub>3</sub>
$6.4 \cdot 10^{-2}$	30	13.0	1.14	APS <sub>4</sub>
$6.4 \cdot 10^{-2}$	240	50.3	1.61	APS <sub>5</sub>
$1.9 \cdot 10^{-2b}$	70	15.8	—	APS <sub>6</sub>

<sup>a</sup> Containing 16.6% (v/v) CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> PPC<sub>2</sub> was used and the volume percentage of CH<sub>2</sub>Cl<sub>2</sub> was 33.3.

PPCs were also used as free radical initiators in the polymerization of styrene in order to prepare APS. Kinetics of the decompositions and of the low conversion polymerization will be published elsewhere<sup>5</sup>. However, representative results are shown in Tab. 2. The concentration of PPC and the polymerization time and temperature play an important role in determining the number of peroxide groups present in the resultant active polymer.

Tab. 3. Cationic polymerization of n-butyl vinyl ether initiated by APSs at 80°C. (20% (v/v) CH<sub>2</sub>Cl<sub>2</sub> are used in order to facilitate the dissolution of the salts).

APS	Salt (M)	Heating time (min)	Conversion (%)
APS <sub>6</sub> (45 g/dl)	Ph <sub>2</sub> I <sup>+</sup> PF <sub>6</sub> <sup>-</sup> ( $2.9 \cdot 10^{-3}$ )	120	70
APS <sub>6</sub> (23 g/dl)	Ph <sub>2</sub> I <sup>+</sup> PF <sub>6</sub> <sup>-</sup> ( $2.9 \cdot 10^{-3}$ )	135	85
APS <sub>6</sub> (25 g/dl)	Ph <sub>2</sub> I <sup>+</sup> PF <sub>6</sub> <sup>-</sup> ( $10^{-2}$ )	135	89
APS <sub>5</sub> (25 g/dl)	AgBF <sub>4</sub> ( $6.4 \cdot 10^{-2}$ )	135	75
APS <sub>1</sub> (30 g/dl)	AgBF <sub>4</sub> ( $8.6 \cdot 10^{-2}$ )	155	48

These polymers were then used as free radical sources, in a similar way to PPC, in the polymerization of BVE. The results are presented in Tab. 3. In the presence of the iodonium salt homo-PBVE chains are expected to form due to the fact that further initiation by phenyl radicals also occurs (reactions (7) and (8)). These additional chains do not consist of initial PS segments. In the case of silver salt polymerization of BVE would be initiated only by macroradicals generated by thermolysis of APS (reactions (5) and (9), R = macroradicals). This behaviour was also evidenced by recent studies<sup>13</sup> on the synthesis of PBVE with photoactive terminal groups. We have therefore focused our studies on the use of the silver salt in order to obtain block copolymers via promoted cationic polymerization. In both cases, however, as the viscosity of the solution increased phase separation was observed, which may be ascribed to the incompatibility of polystyrene and poly(alkyl vinylethers). The polymerization mixture became milky even in dilute solutions (up to 1/1 BVE/CH<sub>2</sub>Cl<sub>2</sub>) as the conversion of BVE increased and the percentage of polystyrene became less. Indeed, according to Kwei et al.<sup>14</sup> polystyrene-poly(methyl vinylether) blends of less than 30 wt.-% polystyrene are thermodynamically unstable towards phase separation. Conformation of possible reaction mechanism and of existence of block copolymer formation was obtained by subjecting a portion of the product, obtained with the AgBF<sub>4</sub> initiation, to diethyl ether extraction over 20 hours. Homopolymer, but not PS, is soluble in diethyl ether, but this treatment removed

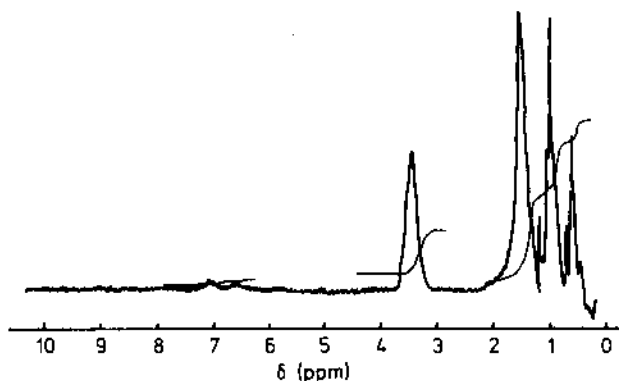


Fig. 1. NMR spectra of the diethyl ether soluble part of the product obtained from the polymerization of *n*-butyl vinylether initiated by active polystyrene in the presence of AgBF<sub>4</sub>.

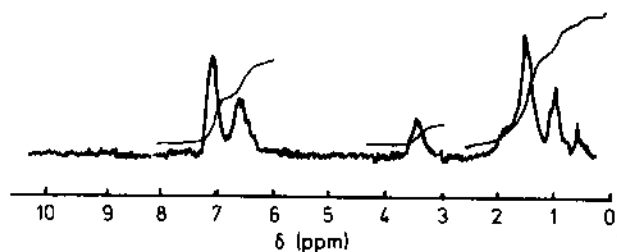


Fig. 2. NMR spectra of the dimethyl ether insoluble part of the product obtained from the polymerization of *n*-butyl vinyl ether initiated by active polystyrene in the presence of  $\text{AgBF}_4$ .

over 80% of the polymer from the sample. NMR data indicate that the soluble part is mainly homo-PBVE consisting negligible amounts of block copolymer structure. As can be seen from Fig. 1 the aromatic ring protons of PS around 6 and 7.06 ppm are insignificant. On the other hand the spec-

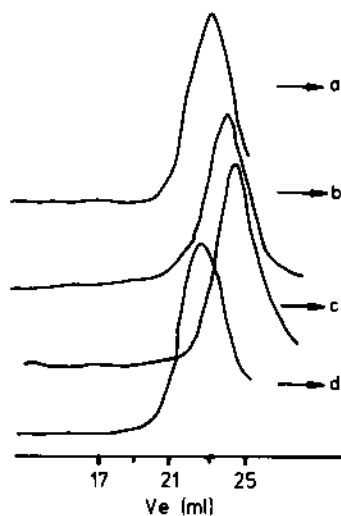
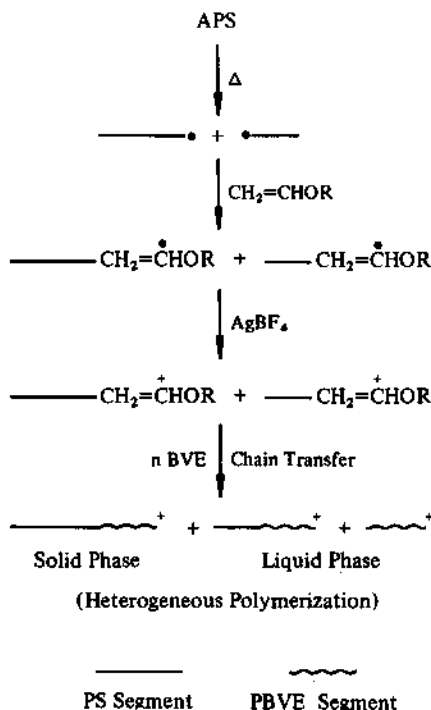


Fig. 3. GPC graphs of (a) the initial active polystyrene,  $M_w$ : 65000, (b) the product obtained from the polymerization of *n*-butyl vinyl ether initiated by the active polystyrene in the presence of  $\text{AgBF}_4$ ,  $M_w$ : 20000, (c) the diethyl ether soluble part of the product,  $M_w$ : 19000, (d) the diethyl ether insoluble part of the product,  $M_w$ : 59500.

trum of the insoluble part displays, in addition to PS bands, three bands at 0.6, 0.98, and 3.35 ppm attributable to butyl ether groups (Fig. 2). The methylene groups of butyl vinylether chains form a broad absorbance overlapping with those of PS in the chemical shift range from 1.1 to 2.2 ppm. These observations support the view that polymerization of BVE proceeds in both phases. Polymerization in the solution phase results mainly in the formation of homo-PBVE whereas block copolymers are formed in the solid phase. It must be pointed out that chain transfer is an important process as far as cationic polymerization of alkyl vinylethers is concerned. In this heterogenous polymerization system initiating species resulting from chain transfer are free of initial PS segments. Presumably, reactions may be generalised as shown in scheme 1.



Scheme 1. Promoted cationic polymerization of *n*-butyl vinylether initiated by active polystyrene in the presence of  $\text{AgBF}_4$ .

The GPC graphs of the initial APS, the mixture of block copolymer and homopolymer, and the diethyl ether soluble and insoluble parts are illustrated in Fig. 3. The molecular weight of the insoluble portion (block copolymer) was slightly lower than that of the initial APS. This is acceptable since relatively short PBVE blocks were added to the scissed APS chains. The high value of the heterogeneity index of the homo-PBVE portion ( $H > 20$ ) is an additional evidence for the effective chain transfer and the presence of oligomeric PBVE chains.

In conclusion, although APS readily initiates the promoted cationic polymerization of BVE leading to block copolymer formation, chain transfer reactions and phase separation are deterrent to the use of this method for the synthesis of block copolymers of BVE. Further studies are now in progress to use cationic susceptible monomers, other than BVE, in which chain transfer reactions are minimized and electron donor radicals can be obtained by an addition mechanism.

We would like to express our thanks to Dr. C. H. Fischer and Mr. R. Zuch (Hahn-Meitner Institut, Berlin, FRG) for the NMR and GPC measurements, respectively. The Alexander von Humboldt Stiftung is also thanked for partial support in form of a grant to Yusuf Yagci.

- <sup>1</sup> C. I. Simionescu, E. Comanita, M. Pastravanu, S. Dumitriu, *Prog. Polym. Sci.* **12** (1986) 1
- <sup>2</sup> E. H. Orhan, I. Yilgor, B. M. Baysal, *Polymer* **18** (1977) 286
- <sup>3</sup> I. Yilgor, B. M. Baysal, *Makromol. Chem.* **186** (1985) 463
- <sup>4</sup> B. Hazer, B. M. Baysal, *Polymer* **27** (1986) 463
- <sup>5</sup> H. Yildirim, B. M. Baysal, manuscript in preparation
- <sup>6</sup> Y. Yagci, *Polymer Commun.* **26** (1985) 7
- <sup>7</sup> Y. Yagci, *Polymer Commun.* **27** (1986) 21
- <sup>8</sup> A. Akar, A. C. Aydogan, N. Talinli, Y. Yagci, *Polym. Bull. (Berlin)* **15** (1986) 293
- <sup>9</sup> A. Ledwith, *Polymer* **19** (1978) 1217
- <sup>10</sup> F. A. Rasoul, A. Ledwith, Y. Yagci, *Polymer* **19** (1978) 1219
- <sup>11</sup> F. A. Rasoul, A. Ledwith, Y. Yagci, *Polym. Bull. (Berlin)* **1** (1978) 1
- <sup>12</sup> J. V. Crivello, J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.* **17** (1979) 977
- <sup>13</sup> Y. Yagci, W. Schnabel, A. Ledwith, submitted to *Eur. Polym. J.*
- <sup>14</sup> T. K. Kwei, T. Nishi, R. F. Roberts, *Macromolecules* **7** (1974) 667