Polymerization of *n*-Butyl Vinyl Ether Photoinitiated by the Initiator System Poly(methyl phenyl silane)/*N*-Ethoxy-2-methylpyridinium Iodide/ ZnI_2 /Benzaldehyde

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ABSTRACT: The cationic polymerization of *n*-butyl vinyl ether (BVE) in dichloromethane solution was initiated at room temperature by a photoinitiator system consisting of poly(methyl phenyl silane), PMPS, *N*-ethoxy-2-methylpyridinium iodide, EMP^+I^- , zinc iodide, ZnI_2 , and benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$. Concerning the initiation mechanism the photolysis of PMPS at wavelengths exceeding 340 nm was assumed to yield silyl radicals, the oxidation of which by EMP^+ ions yields silyl cations. The latter reacts readily with I^- , the counterion of EMP^+ ion, thus producing terminal Si–I groups at the polysilane chains. Si–I groups can initiate the polymerization of BVE in the presence of ZnI_2 and benzaldehyde. The formation of block copolymers consisting of MPS and BVE repeating units was confirmed by solvent extraction and ^1H NMR analysis.

KEY WORDS Polysilane Photolysis / Cationic Polymerization / Electron Spin Resonance / Electron Transfer / *n*-Butyl Vinyl Ether / Transformation Polymerization / Pyridinium Salts /

The design and synthesis of polymers with novel properties are important for broadening technical applications. Appropriate methods frequently employed for this purpose are based on the preparation of block copolymers with the aid of low-cost monomers.¹ The preparation of block copolymers by transformation reactions according to Scheme 1 may enlarge the number of possible monomer combinations and lead to materials with novel properties.² Recently, we succeeded in the radical/cation transformation polymerization of vinyl monomers by a one-step method and in this way block copolymers consisting of both radically and cationically polymerized segments were prepared (Scheme 2).³ Radical/cation transformation is realized by oxidizing propagating macroradicals with appropriate electron acceptors. The terminal cations at the polymer chains thus produced initiate the polymerization of a cationically polymerizable monomer present in the system from the very beginning of the experiment. In this way a block copolymer is formed.³ Accordingly, macroradicals pro-

duced by main-chain scission of a linear polymer can undergo radical/cation transformation provided a proper acceptor is available.

Polysilanes are photosensitive polymers that readily form terminal silyl radicals by main-chain cleavage upon UV irradiation. Therefore, they act as photoinitiators for the free radical polymerization of vinyl monomers.⁴ The photopolymerization of cationically polymerizable monomers is possible when initiator systems consisting of a polysilane and an electron acceptor capable of oxidizing silyl radicals are used.⁵ In a previous paper we studied the mechanism of the cationic polymerization of cyclohexene oxide, CHO, initiated by an initiator system consisting of poly(methyl phenyl silane) (PMPS), and *N*-ethoxy-2-methylpyridinium salt, EMP^+X^- .⁶ By ESR measurement it was confirmed that the photolysis of PMPS at $\lambda_{\text{inc}} > 340$ nm yields silyl radicals that are oxidized by EMP^+ ions as depicted by Scheme 3. The resulting silyl cations was only weakly reactive toward CHO and it was concluded that mainly species other than silyl cations initiate the polymerization of CHO. In a system containing $\text{EMP}^+\text{PF}_6^-$ silyl cations were found to react readily with PF_6^- ions to form stable Si–F bonds (see Scheme 4), and PF_5 generated simultaneously was thought to initiate the homopolymerization of

Scheme 1.

Mr : radically polymerizable monomer
 Mc : cationically polymerizable monomer

Scheme 2.

Scheme 3.

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EXPERIMENTAL

Materials

The syntheses of PMPS ($M_w: 3.41 \times 10^4$) and EMP^+I^- were reported previously.⁶ BVE (Nacalai Tesque Inc., Japan) was washed with 5% NaOH aqueous solution, dried over Na_2SO_4 and CaH_2 , and distilled. Commercially available dichloromethane and benzaldehyde were dried over CaH_2 and distilled. Zinc iodide was dried under vacuum at 100°C for three hours.

Polymerization

Dichloromethane solutions containing PMPS, EMP^+I^- , ZnI_2 , $\text{C}_6\text{H}_5\text{CHO}$, and BVE were put in quartz ampoules and irradiated with monochromatic light ($\lambda_{\text{inc}} = 345 \text{ nm}$) at room temperature. Prior to irradiation the solutions were purged with argon to remove oxygen. The light source was a xenon lamp (Ushio DSB-501A) used with a monochromator (JASCO CT-10). After irradiation, the reaction mixture was poured into excess methanol containing a small amount of ammonia. The polymer precipitated thereby (newly formed polymer and residual PMPS) was extracted with *n*-hexane for 15 hours. After concentrating the extract with an evaporator, it was diluted with THF and the polymer was precipitated with methanol. The *n*-hexane-insoluble fraction was dissolved in THF and the polymer was precipitated with methanol.

Characterization of Polymers

¹H-NMR Spectra. The composition of the polymers was determined by ¹H NMR spectroscopy. Spectra were recorded with a JEOL JNM EX-270 spectrometer at 30°C using CDCl_3 as solvent.

Molar Mass. The number and weight average molar mass, M_n and M_w , and molar mass distribution were roughly estimated by size exclusion chromatography, SEC, using a high-speed liquid chromatography system (TOSOH CCP&8010 series) equipped with a TSK gel column. THF served as the eluent. The flow rate was 0.8 mL min^{-1} . Polystyrene standard calibration was done.

RESULTS AND DISCUSSION

Polymerization

Results of the polymerization of BVE in the presence of EMP^+I^- and PMPS are shown in Table I along with those for the control. BVE polymerized readily in dichloromethane solution containing PMPS, EMP^+I^- , ZnI_2 , $\text{C}_6\text{H}_5\text{CHO}$, and BVE. However, BVE did not polymerize in the absence of any one of these substances.

Characterization of Block Copolymers

According to the initiation mechanism discussed above, block copolymers consisting of PMPS and PBVE blocks should be formed in the photoinitiator system PMPS, EMP^+I^- , $\text{C}_6\text{H}_5\text{CHO}$, ZnI_2 , and BVE. Experimental conditions favorable for the formation of block copolymers were high PMPS concentration and relatively short irradiation time. Typical reaction conditions appropriate for the generation of block copolymers with

Scheme 4.

Scheme 5.

Scheme 6.

CHO .⁶ Similarly, in a system containing EMP^+I^- , stable Si-I bonds should be formed. Vinyl ethers can be polymerized by an initiator system consisting of trimethylsilyl halide, Me_3SiX , aldehyde and zinc halogenide, ZnX_2 , as illustrated by Scheme 5.⁷ Accordingly, it was assumed that terminal Si-I groups in PMPS, generated by the reaction of terminal silyl cations with I^- ions, can initiate the polymerization of vinyl ethers in the presence of ZnI_2 and $\text{C}_6\text{H}_5\text{CHO}$ (Scheme 6). The results presented below substantiate this assumption. BVE was polymerized and block copolymers consisting of MPS and BVE blocks were formed.

Table I. Photopolymerization of *n*-butyl vinyl ether (BVE)^a (Initiator system: PMPS/EMP⁺I⁻, C₆H₅CHO, and ZnI₂)

No.	BVE	EMPI	PMPS	C ₆ H ₅ CHO	ZnI ₂	Time	Conv.	<i>M_w</i>	PMPS/BVE
	M	mM	mM	M	mM	min	%	× 10 ⁻⁴	(molar ratio, unit)
1	1.32	20.1	33.2	0.69	15.7	90	53	2.17	1:20
2	1.32	20.1	33.2	0	0	90	~0		
3	1.32	20.1	0	0.69	15.7	90	~0		
4	1.32	20.1	33.2	0.69	0	90	~0		
5	0.66	20.1	270	0.69	15.7	60	51	1.77	1:1.3

^a λ_{inc} = 345 nm, solvent, CH₂Cl₂; temperature, 20°C, under nitrogen in a glass cell. **Scheme 7.** **Figure 1.** ¹H NMR spectrum of the *n*-hexane-soluble fraction in CDCl₃ solution.

a balanced composition of sufficiently long PMPS and PBVE segments are shown in Table I under run 5. According to Scheme 7, the product polymer obtained was extracted with *n*-hexane, a solvent for PBVE and nonsolvent for PMPS. The composition of the two fractions was determined from the ¹H NMR spectra shown in Figures 1 and 2. Accordingly, the *n*-hexane-soluble fraction contained a small amount of PMPS; the molar ratio (in terms of repeating units) was PMPS:PBVE=1:13. The presence of PMPS in the *n*-hexane-soluble fraction is evidence for the formation of the block copolymer since homo-PMPS is insoluble in *n*-hexane. The size exclusion chromatogram obtained with this fraction (chromatogram b in Figure 3) consists of a peak at relatively high molar mass attributed to the block copolymers and shoulder at lower molar mass assigned to homo-PBVE, as confirmed by chromatography using UV detector at 254 nm. The composition of the *n*-hexane-insoluble fraction indicated a molar ratio PMPS:

Figure 2. ¹H NMR spectrum of the *n*-hexane-insoluble fraction in CDCl₃ solution. **Figure 3.** SEC chromatograms of polymer prepared by the polymerization of the system PMPS/BVE with EMP⁺I⁻, C₆H₅CHO, and ZnI₂ under the conditions in Table I for run 5. (a) crude polymer; (b) *n*-hexane-soluble fraction; (c) *n*-hexane-insoluble fraction; (d) prepolymer of PMPS.

PBVE=1:0.24. This fraction thus also contains some extent block copolymer. Since blends of the homopolymers PMPS and PBVE were completely fractionated into the components by *n*-hexane extraction, this suggests that PBVE is chemically attached to PMPS.

By appropriate reaction conditions, a copolymer consisting of PMPS and PBVE blocks is formed when the photopolymerization of BVE is initiated by the initiator system, PMPS, EMP⁺I⁻, C₆H₅CHO, and ZnI₂.

CONCLUSIONS

This paper reports the photopolymerization of BVE initiated by the initiator system, PMPS, EMP⁺I⁻, C₆H₅CHO, and ZnI₂. The formation of block co-

polymer, Poly(MPS-*b*-BVE) was confirmed by separating block and homopolymers by extraction and characterizing the fractions by ^1H NMR measurement. On the basis of ESR results reported elsewhere⁶ the following mechanism is applicable: the photolysis of PMPS at $\lambda_{\text{inc}} > 340$ nm yields silyl radicals that is oxidized by EMP^+ ions to form silyl cations. The latter readily react with I^- , the counter ion of EMP^+ ion, to produce terminal Si-I groups at the PMPS chains. The Si-I groups initiate the polymerization of BVE in the presence of $\text{C}_6\text{H}_5\text{CHO}$ and ZnI_2 .

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