

Synthesis of AB and ABA Type Block Copolymers of Vinyl Chloride Using Iniferter Technique

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ABSTRACT: The photopolymerization of vinyl chloride (VC) with benzyl *N,N*-diethyldithiocarbamate (BDC) or *p*-xylylene bis(*N,N*-diethyldithiocarbamate) (XDC) was carried out in 1,2-dichloroethane at 30 °C. From the ¹H NMR spectra, these poly(vinyl chloride)s (PVC) were found to contain mono- or di-functional polymers which can be used for synthesizing the AB type or ABA type block copolymers, respectively. The photocopolymerization of the mono-functional PVC with styrene (St) or vinyl acetate (VAc) was carried out in cyclohexanone at 30 °C. The obtained copolymers were the AB type block copolymers of VC with St or VAc. The photocopolymerization of the di-functional PVC with St in cyclohexanone at 30 °C gave an ABA type block copolymer of VC and St.

KEY WORDS Vinyl Chloride / Iniferter / Block Copolymer / Living Polymerization / Styrene / Vinyl Acetate /

Copolymers often have significant features different from those of homopolymers and are expected to be new materials in the fields of elastomers and paints. PVC is a commodity polymer which can be used in the fields of pipe and films, and the copolymers of VC with other monomers have been synthesized. For example, the copolymerizations of VC with methyl methacrylate,¹ VAc,² and vinylidene chloride³ have been reported. The VC content increases by adding Lewis acids such as SnCl₄ during the copolymerization with acrylic or methacrylic esters.⁴ During the copolymerization of VC with ethylene, the ethylene content increases with the addition of AgNO₃ solution.⁵ These copolymers possess a random monomer distribution. Furukawa *et al.* synthesized the alternating copolymer of VC with acrylonitrile using ethylaluminum dichloride.⁶ However, a block copolymer of VC has not yet been synthesized.

Living radical polymerization is a useful method for block copolymer synthesis.^{7–14} One of the synthetic methods is the iniferter technique.^{7–9} This is a method using a compound with a weak bond such as the C–S and S–S bond as the initiator. An AB type block copolymer can be synthesized from the mono-functional polymer obtained by the photopolymerization of St with benzyl *N,N*-diethyldithiocarbamate (BDC) as the initiator.^{7,8} Analogously, an ABA type block copolymer can be synthesized using the di-functional polymer prepared with *p*-xylylene bis(*N,N*-

N-diethyldithiocarbamate) (XDC) as the initiator.^{8,9} These processes are shown in Scheme 1.

In this study, in order to synthesize the AB and ABA type block copolymers, the photopolymerizations of VC with BDC or XDC were first carried out in 1,2-dichloroethane at 30 °C, followed by the copolymerizations of St or VAc with the mono-functional or di-functional PVC.

EXPERIMENTAL

Materials

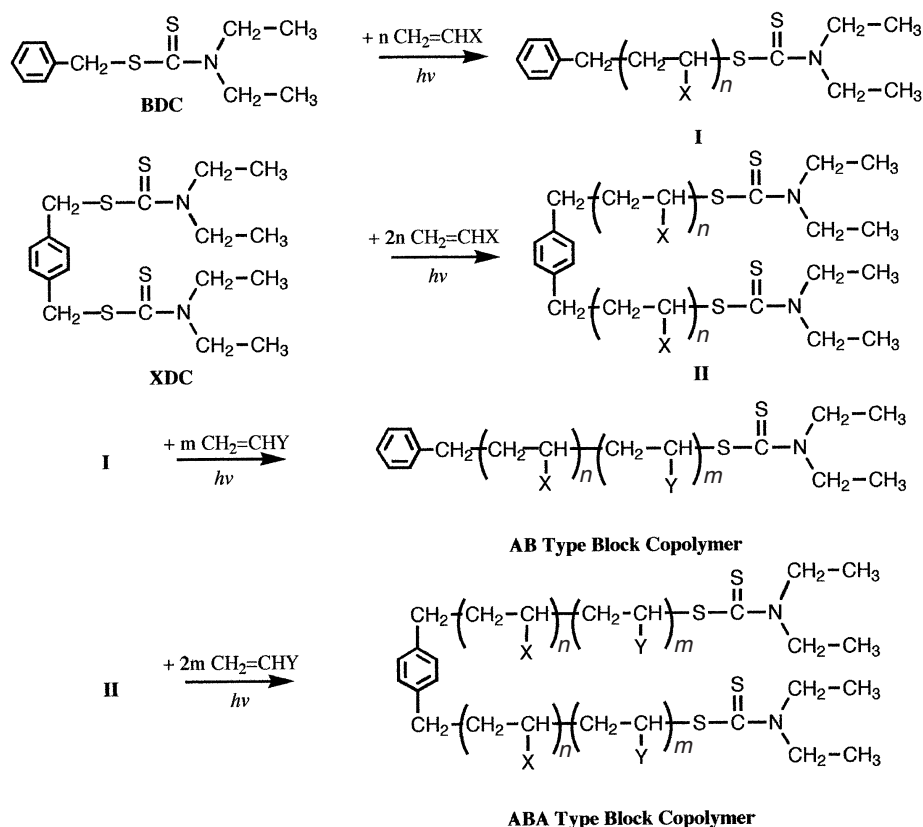
VC purchased from the Takachiho Chemical Co. was used as received. BDC was prepared from benzyl chloride (KISHIDA; purity > 99%) and sodium *N,N*-diethyldithiocarbamate (KISHIDA; purity > 92%) in ethanol for 24 h in the dark according to the literature.⁸ BDC was purified by silica gel column chromatography with diethyl ether as an eluent and then distilled (130 °C/2 mmHg). XDC was similarly prepared from *p*-xylylene dichloride (Wako; purity > 98%),⁸ and recrystallized from methanol (mp : 84 °C). Solvents, St, and VAc were purified by distillation in the presence of CaH₂ before use. The other reagents were purified by the usual methods.

Polymerization and Copolymerization

Polymerization was performed in the presence of BDC or XDC in a sealed glass tube under a nitrogen

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Scheme 1.

atmosphere equipped with a three-way stopcock as follows. BDC or XDC and a solvent were added to the sealed glass tube using a hypodermic syringe at room temperature, and then VC was added to the sealed glass tube at $-78\text{ }^{\circ}\text{C}$ by vacuum distillation. The polymerization reaction was initiated by irradiating UV light using a Riko UVL-400HA UV lamp at $30\text{ }^{\circ}\text{C}$. The polymerization reaction was terminated by stopping the UV light irradiation. The obtained PVC was precipitated into a large amount of methanol, separated by centrifugation, and dried under vacuum at $60\text{ }^{\circ}\text{C}$ for 12 h.

The copolymerization of St or VAc with the obtained PVC was analogously carried out like the polymerization of VC. The obtained copolymer was precipitated in methanol, separated by centrifugation, and dried under vacuum at $60\text{ }^{\circ}\text{C}$ for 12 h. The homopolymers were then separated by extracting with boiling cyclohexane or acetonitrile for 12 h.

Measurements

^1H NMR spectra were obtained using a Varian Gemini 2000 spectrometer (400 MHz for ^1H). The size-exclusion chromatographic (SEC) analysis of the polymers was performed using polystyrene standards on a JASCO PU-980 chromatograph equipped with a JASCO RI-930 detector and TSK gel GMH_{HR}-H and G3000H_{HR} columns (eluent; THF, flow rate; 1.0 mL min^{-1} , temperature; $40\text{ }^{\circ}\text{C}$). The molecular

Table I. Photopolymerization of VC with BDC or XDC in 1,2-dichloroethane at $30\text{ }^{\circ}\text{C}$ ^a

Run	Initiator	Time h	Conv./% ^b	M_n^c	M_w/M_n^c
1	BDC	24	5.6	4900	1.69
2		45	11.0	5100	1.66
3		70	17.3	5400	1.71
4		144	21.7	7200	1.65
5	XDC	24	4.9	6800	1.68
6		70	5.9	7500	1.46
7		144	12.3	10900	1.44

^a[VC] 7 mol L^{-1} (0.035 mol), [initiator] 39.5 mmol L^{-1} (0.20 mol), ^bMeOH-insoluble part. ^cDetermined by SEC (polystyrene standard) of original polymers in THF.

weight (M_n) and its distribution (M_w/M_n) were determined from the UV peak (254 nm UV) of the polymer from the SEC.

RESULTS AND DISCUSSION

Synthesis of End-reactive PVC

The photopolymerization of VC with BDC or XDC was performed in 1,2-dichloroethane at $30\text{ }^{\circ}\text{C}$ (Table I). The polymerization proceeded homogeneously at first, but the system became heterogeneous after 3 h and the polymerization solution changed from colorless to dark brown. The obtained polymer had a dark brown

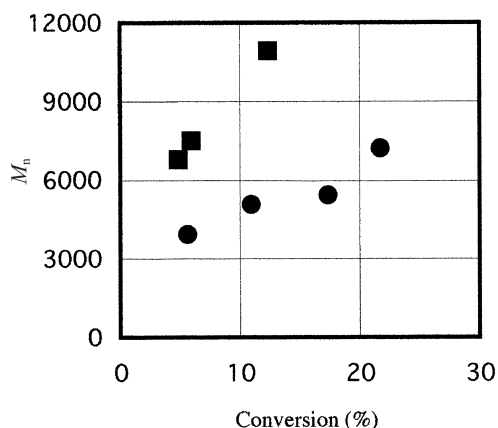


Figure 1. Plots of conversion vs. M_n in photopolymerizations of VC with BDC (●) or XDC (■) in 1,2-dichloroethane at 30 °C; [VC] 7 mol L⁻¹ (0.035 mol), [initiator] 39.5 mmol L⁻¹ (0.20 mmol).

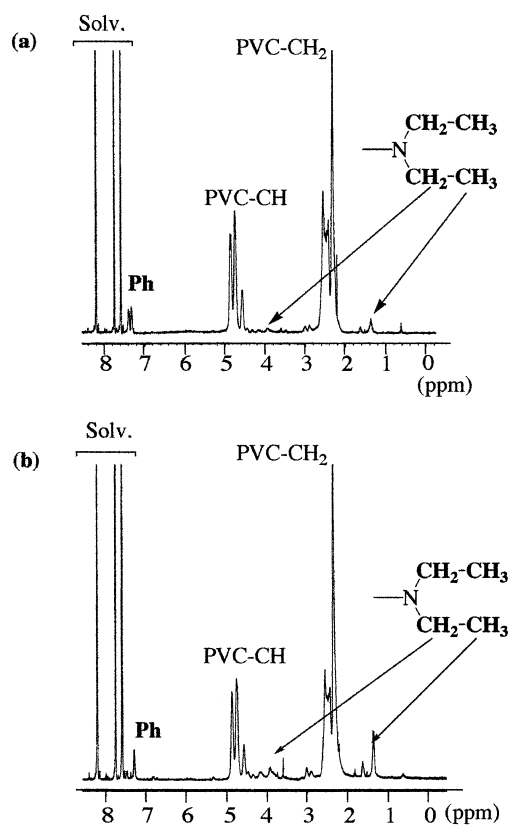


Figure 2. 400 MHz ¹H NMR spectra of PVC obtained with (a) BDC or (b) XDC [in nitrobenzene-*d*₅ at 60 °C].

color. Figure 1 shows the conversion- M_n curves of these photopolymerizations. The photopolymerizations were different from the living radical polymerization of St with BDC or XDC, in which the M_n linearly increased with conversion.⁷⁻⁹ The molecular weight of the obtained PVC did not increase linearly with conversion, because the propagating radical with a high reactivity was not efficiently trapped by the diethyldithiocarbamate radical, and the termination and chain transfer reactions occurred during the photopolymerization of VC with BDC or XDC. The ¹H NMR spectra of

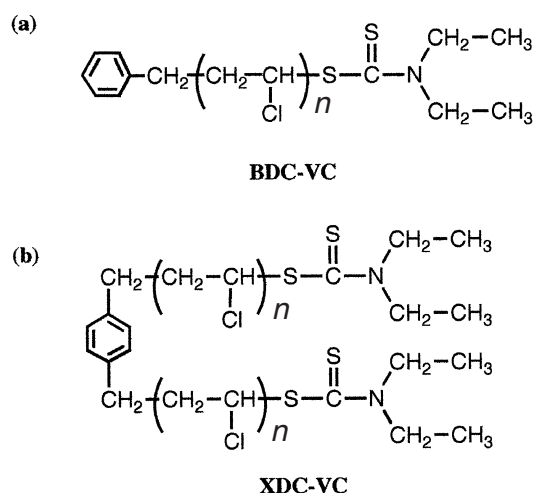


Figure 3. The structures of the PVCs obtained with (a) BDC or (b) XDC in 1,2-dichloroethane at 30 °C under photoirradiation.

Table II. Photopolymerization of St with BDC-VC in cyclohexanone at 30 °C^a

Run	Time h	Yield/g ^b	M_n^c	M_w/M_n^c
1	3	0.09	37800	1.97
2	24	0.26	98500	1.38
3	70	0.32	152500	1.49

^a[St] 7 mol L⁻¹ (0.028 mol), [BDC-VC (Run 1 in Table I)] 15.1 mg. ^bMeOH-insoluble part. ^cDetermined by SEC (polystyrene standard) of original polymers in THF.

the polymers (Run 1 and Run 5 in Table I) are shown in Figure 2. The peaks assigned to the initiator fragment are observed beside the peaks due to PVC; the phenyl, methylene, and methyl groups in the terminal are observed at 7.4 ppm, 4 ppm, and 1.4 ppm, respectively. Therefore, the PVCs should have the structures as shown in Figure 3. From the intensities of the phenyl peak to the end methylene peak in Figure 2, the number of (C₂H₅)₂NCSS- end groups per one PVC chain was found to be 0.7 for BDC and 1.6 for XDC. These values are lower than the values 1 and 2 for the living polymerization of VC with BDC or XDC, respectively. These lower values are ascribed to the termination and transfer reaction of the VC radical. The obtained BDC-VC and XDC-VC having a (C₂H₅)₂NCSS- end group are end-reactive polymers, which can be used as polymeric initiators.

Synthesis of AB Type Block Copolymer of VC with St or VAc

The mono-functional photoinitiator (BDC-VC) was used to prepare the AB type block copolymers of VC and St (PVC-*block*-PSt) or VAc (PVC-*block*-PVAc). The copolymerization of BDC-VC and St was carried out in cyclohexanone at 30 °C under UV irradiation (Table II). On the other hand, the polymeriza-

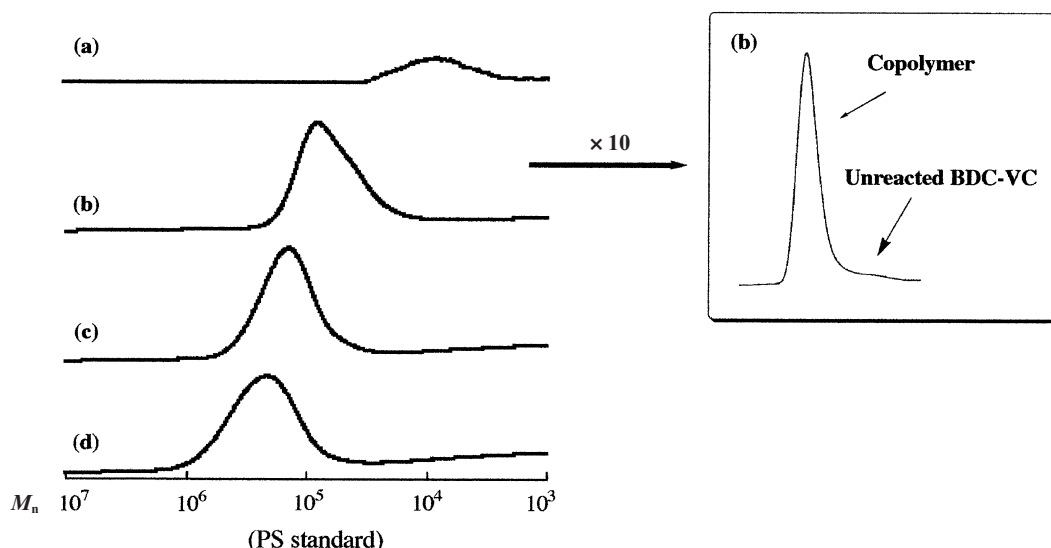


Figure 4. SEC curves (UV 254 nm) of polymers of St photoinitiated with BDC-VC in cyclohexanone at 30 °C; [St] 7 mol L⁻¹ (0.035 mol), [BDC-VC (Run 1 in Table I)] 15.1 mg; polymerization time (a) 0 h (BDC-VC), (b) 3 h, (c) 24 h, (d) 70 h.

tion of St without BDC-VC under a similar condition did not proceed. Therefore, for this copolymerization, BDC-VC was necessary as an initiator. BDC-VC was dissolved in cyclohexanone to give a dark brown solution, and then, St was added. The reaction homogeneously proceeded. The SEC analysis of the obtained polymers is depicted in Figure 4. The molecular weights of the polymers increased with the polymerization time as well as in the living polymerization of St with BDC or XDC. However, the SEC curve (b) in Figure 4 had a small peak in the low molecular weight region besides the peak due to the copolymer peak. From the ¹H NMR spectrum of the PVC obtained with BDC (BDC-VC in Figure 2), the 70% BDC-VC has the (C₂H₅)₂NCSS- group at the terminal, but 30% BDC-VC does not. Therefore, this small peak may be assigned to the unreacted BDC-VC without the (C₂H₅)₂NCSS- group at the terminal. From the SEC curves in Figure 4, the molecular weight of the copolymer increased with polymerization time, though there existed a small amount of unreacted BDC-VC in the low molecular weight region. These results indicate that the St polymerization was initiated by BDC-VC and proceeded in a living manner.⁷

The products may contain homopolymers, PVC and PSt, besides the block copolymer. However, it was difficult to fractionate a small amount of the unreacted PVC and block copolymer. The PSt homopolymer (10%) was extracted with boiling cyclohexane for 12 h. The ¹H NMR spectra of the cyclohexane-soluble and -insoluble parts are shown in Figure 5. The cyclohexane-soluble part shows only the signals of polystyrene, and the cyclohexane-insoluble part shows the signals of polystyrene and PVC. Therefore, this

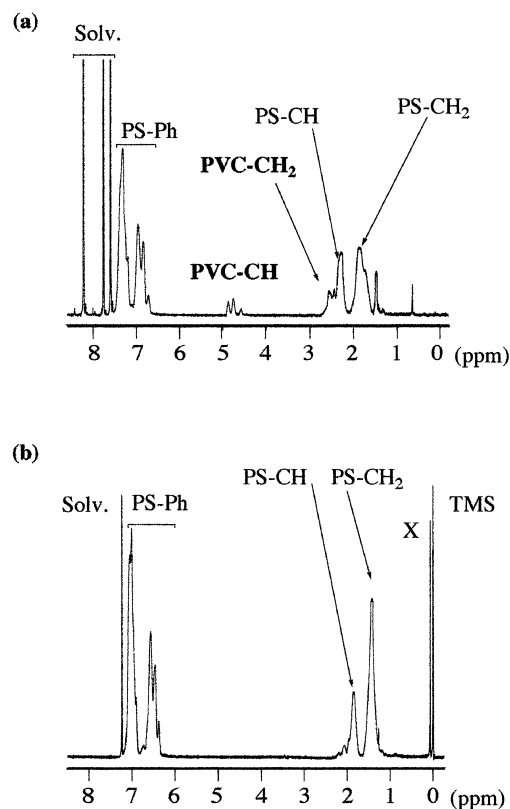


Figure 5. 400 MHz ¹H NMR spectra of the products obtained in BDC-VC/St system; (a) cyclohexane-insoluble part [in nitrobenzene-*d*₅ at 60 °C], (b) cyclohexane-soluble part [in CDCl₃ at 60 °C].

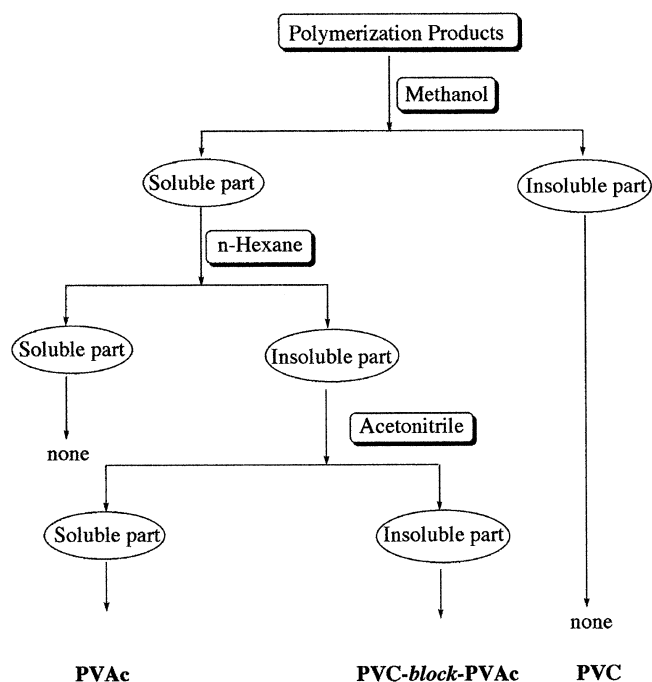
cyclohexane-insoluble part must be the block copolymer of VC and St (PVC-*block*-PSt), though this part contains a small amount of the PVC homopolymer.

The copolymerization of BDC-VC and VAc was also carried out in cyclohexanone at 30 °C under UV irradiation (Table III). The fractionation of the product

Table III. Photopolymerization of VAc with BDC-VC in cyclohexanone at 30 °C^a

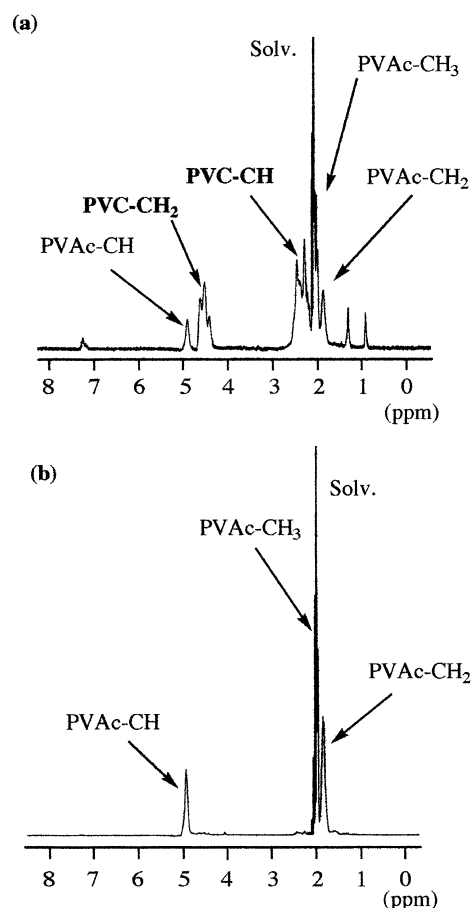
Run	Time/h	Yield/g ^b	Acetonitrile-soluble part			Acetonitrile-insoluble part		
			Yield/g ^c	M_n^d	M_w/M_n^d	Yield/g ^c	M_n^d	M_w/M_n^d
1	24	0.080	0.059	11500	1.66	0.021	10900	1.44
2	70	0.125	0.101	11900	1.71	0.024	12400	1.41

^a[VAc] 7 mol L⁻¹ (0.021 mol), [BDC-VC (Run 1 in Table I)] 27.2 mg. ^bHexane-insoluble part. ^cHexane-insoluble and acetonitrile-soluble part. ^dDetermined by SEC (polystyrene standard) of original polymers in THF. ^eHexane-insoluble and acetonitrile-insoluble part.

**Figure 6.** Fractionation of the products obtained by photopolymerization of VAc by BDC-VC in cyclohexanone at 30 °C.

was performed as described in Figure 6. The unreacted PVC without the (C₂H₅)₂NCSS- group at the terminal should exist similar to the photocopolymerization of BDC-VC and St. However, the amount of this PVC may be too small to be precipitated in a large amount of methanol. On the other hand, the formation of PVAc and PVC-*block*-PVAc was confirmed through fractionation. The molecular weight of the copolymer did not linearly increase with polymerization time (3 h and 70 h), which is different from the BDC-VC / St system. It has been reported that the polymerization of VAc with BDC as an initiator does not proceed in a living manner¹⁵ because of the termination and chain transfer reactions.

The ¹H NMR spectra of the acetonitrile-soluble and -insoluble fractions are shown in Figure 7. The acetonitrile-soluble part exhibits only the signal due to PVAc, and the acetonitrile-insoluble part exhibits the signals due to the VAc and VC sequences. Therefore, this acetonitrile-insoluble part must be the block copolymer of VC and VAc (PVC-*block*-PVAc).

**Figure 7.** 400 MHz ¹H NMR spectra of the products obtained in BDC-VC/VAc system; (a) acetonitrile-insoluble part, (b) acetonitrile-soluble part [in acetone-*d*₆ at room temperature].

Synthesis of ABA Type Block Copolymer of VC with St

The di-functional photoinitiator (XDC-VC) is expected to give an ABA type block copolymer. The synthesis of the ABA (PSt-PVC-PSt) type block copolymer of VC and St was examined. The copolymerization of XDC-VC and St was carried out in cyclohexanone at 30 °C under UV irradiation (Table IV). The copolymerization proceeded homogeneously as well as during the copolymerization of BDC-VC with St or VAc. The molecular weights of the copolymers increased as the copolymerization proceeded similar to the copolymerization of BDC-VC and St.

The obtained product may contain PVC and PSt homopolymers in addition to the block copolymer.

Table IV. Photopolymerization of St with XDC-VC in cyclohexanone at 30 °C^a

Run	Time h	Yield/g ^b	M_n^c	M_w/M_n^c
1	3	0.110	46600	1.84
2	6	0.186	66700	1.66
3	24	0.319	78900	1.85

^a[St] 7 mol L⁻¹ (0.028 mol), [XDC-VC (Run 5 in Table I)] 15.1 mg. ^bMeOH-insoluble part. ^cDetermined by SEC (polystyrene standard) of original polymers in THF.

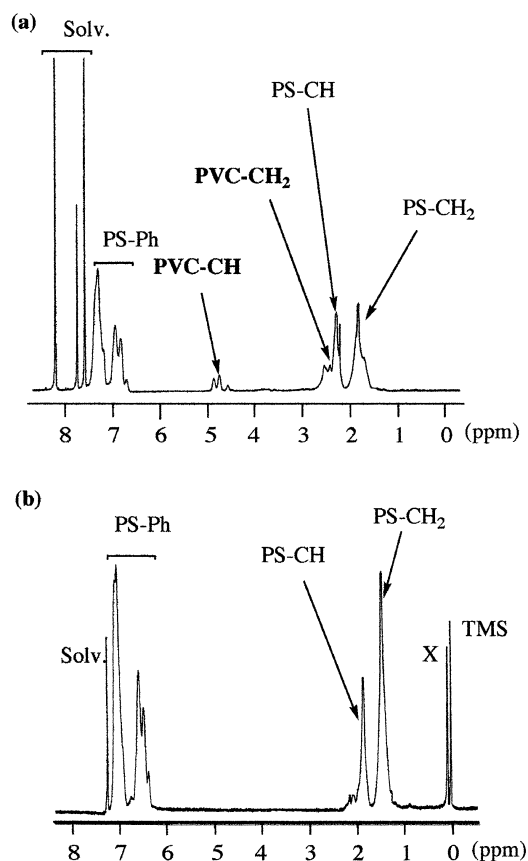


Figure 8. 400 MHz ¹H NMR spectra of (a) cyclohexane-insoluble part [in nitrobenzene-*d*₅ at 60 °C], (b) cyclohexane-soluble part [in CDCl₃ at 60 °C] in the products in the polymerization of St by XDC-VC.

Therefore, removal of the homopolymers was examined. However, it was difficult to fractionate the unreacted PVC from the block copolymer as well as in the polymerization system of BDC-VC and St. On the other hand, the PSt homopolymer (25%) was extracted by refluxing in cyclohexane for 12 h. The ¹H NMR spectra of the cyclohexane-soluble and -insoluble fractions are shown in Figure 8. The cyclohexane-soluble part shows the signals of only polystyrene, and the cyclohexane-insoluble part shows the signals of polystyrene and PVC. This cyclohexane-insoluble part must be the block copolymer of VC and St (PVC-*block*-PSt), though this part contains a small amount of the PVC homopolymer.

CONCLUSIONS

The syntheses of the block copolymers of VC with St or VAc were examined. VC was polymerized with benzyl *N,N*-diethyldithiocarbamate (BDC) or *p*-xylylene bis(*N,N*-diethyldithiocarbamate) (XDC) which gave a mono-functional (BDC-VC) or di-functional PVC (XDC-VC), respectively. BDC-VC photoinitiated the polymerization of styrene and vinyl acetate in cyclohexanone at 30 °C to afford the AB type block copolymers. The polymerization of St by BDC-VC proceeded in a living manner. The di-functional XDC-VC also photoinitiated the polymerization of styrene in cyclohexanone at 30 °C affording an ABA type block copolymer. This polymerization also proceeded in a living manner.

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