

# Graft Copolymerization by Iniferter Method; Structural Analyses of Graft Copolymer by Glass Transition Temperature

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## Synopsis

Since 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) polymer easily cleaves at the C—S bond and generates benzyl radical, graft copolymerization of methyl methacrylate (MMA) or 4-vinylpyridine (VPy) onto VBDC polymer is easily performed by UV irradiation. The structural analyses of the graft copolymer are performed through glass transition temperature measurements. The graft copolymers of MMA have one  $T_g$  and VPy graft copolymers have two  $T_g$ 's arising from the main and side chains. It becomes clear that the mode of side chains propagation is significantly different for each of the second monomers used.

## INTRODUCTION

A photoiniferter technique is one of the graft copolymerization methods, and *N,N*-diethyldithiocarbamate derivatives have been reported to act as a photoiniferter for living radical polymerization in homogeneous systems.<sup>1</sup> The use of an iniferter has been found to be effective for the syntheses of various functional block and graft copolymers.<sup>2,3</sup> An effective graft copolymerization method uses 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) polymer as a polymeric photoiniferter, where the second monomer is easily graft copolymerized photochemically.<sup>3</sup>

The procedure for this graft copolymerization is characteristically easy. In comparison with the usual troublesome macromonomer method,<sup>4</sup> this free radical method results in a facile polymerization of the functional monomer, which cannot be polymerized by ionic polymerization. In addition, it is difficult to construct graft polymer by the classical chain transfer methods<sup>5</sup> or emulsion polymerization method.<sup>6</sup> However, we are able to construct the desired structure of graft copolymers by this iniferter method.

By this graft copolymerization, the length of grafting side chain increases with polymerization time.<sup>7</sup> Therefore, it is possible to synthesize a block copolymer on the grafted side chain by adding a third monomer.<sup>8</sup> These graft copolymerization methods are very effective for the construction of functional polymers.

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Since the mode of side chains propagation is extremely complicated in this system, it is very difficult to analyze exactly the structure of the graft copolymer. On the other hand, the glass transition temperature ( $T_g$ ) of the graft copolymers are known to be influenced by the chemical structure and the method of attachment of the graft chain onto the main chain.<sup>9-11</sup> Therefore, we utilized the  $T_g$  as an indicator of the graft copolymer structures.

## EXPERIMENTAL

### Materials

VBDC was synthesized as in our earlier report.<sup>3</sup> Styrene (St), MMA, and VPy were purified by the ordinary methods and distilled just before use. Sodium *N,N*-diethyldithiocarbamate was supplied from Ouchi-Shinko Co. Ltd. Other reagents and solvents were used after purification.

### Synthesis of Polymeric Photoiniferter

The VBDC homopolymer and St-VBDC copolymers which were used as polymeric photoiniferters were prepared by the usual radical polymerizations using 2,2'-azobisisobutyronitrile (AIBN) in benzene at 60°C in dark. Polymerizations were carried out in degassed sealed Pyrex tubes. The obtained polymers were purified by reprecipitation from the benzene-*n*-hexane system. The content of VBDC units in the copolymers was determined by elemental analyses of sulfur, carbon, and nitrogen.

### Graft Copolymerization

The graft copolymerizations of various monomers onto polymeric photoiniferter were carried out in sealed Pyrex tubes with shaking at 30°C under irradiation from a Toshiba SHL-100UV lamp at a distance of 3 cm. After polymerization for a given time, the contents of the tube were poured into large amounts of suitable precipitants to isolate the whole polymers. The separations of the resultant polymer mixtures were carried out by extracting with suitable solvents, i.e., cyclohexane, acetonitrile, and methanol for VBDC polymers, homoPMMA, and homoPVPy, respectively. Graft copolymers were extracted with chloroform after the above extractions in order to separate the insoluble crosslinked polymers.

Photopolymerizations of MMA or VPy were also carried out in the presence of VBDC as a photoiniferter under UV irradiation from a distance of 10 cm. The detailed polymerization procedures were the same as that for the above graft copolymerizations. The intrinsic viscosities  $[\eta]$  and reduced viscosities were measured in chloroform at 30°C.  $T_g$ 's were determined on a Rigaku PTC-10A differential scanning calorimeter at a scan rate of 10°C/min (see Fig. 2).

## RESULTS AND DISCUSSION

### Synthesis of Graft Copolymer

In the previous paper,<sup>3</sup> we reported that VBDC behaved similarly to St in radical polymerization, and its dithiocarbamoyl group was cleaved easily by

UV irradiation. However, spectroscopic evidence revealed that the photosensitive dithiocarbamoyl groups did not react during the radical polymerization in the presence of AIBN.

In order to avoid the deactivation and coupling of growing end groups in these polymerizations, we added tetraethylthiuram disulfide (TD), which generated the same thiyl radical as VBDC under UV irradiation. A typical example of the purification procedure of homoVBDC-*g*-VPy copolymer is represented in the flow chart (Fig. 1).

### Structural Evaluation of Graft Copolymer

The  $T_g$  of random copolymer usually falls between that of the corresponding homopolymers.<sup>9</sup> However, it has been found that block or graft copolymer which sufficiently homogeneous long chain segments exhibit  $T_g$ 's for each homopolymer rather than single intermediate values.<sup>12</sup>

Cameron and Chisholm<sup>10,11</sup> reported that the microphases were well developed and the phase boundaries were reasonably sharp in copolymers with long graft chains but low graft density. However, with short graft chains at high density, there was considerable penetration of each polymer domains into each other resulting in the more diffuse phase boundaries. Therefore, we evaluated the  $T_g$  of the graft copolymer to clarify the structure of the graft copolymer.

### Graft Copolymerization of MMA onto HomoPVBDC

In the previous paper,<sup>3</sup> we reported that the photopolymerization of MMA using monomeric VBDC proceeded via a living radical mechanism. Similarly, by a photopolymerization of MMA using VBDC homopolymer graft copolymers

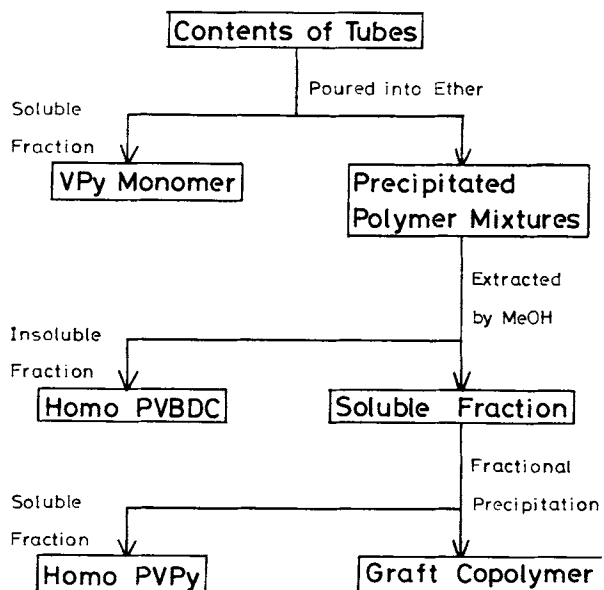


Fig. 1. The purification procedure of homo-VBDC-*g*-VPy copolymer.

TABLE I  
Graft Copolymerization of MMA onto Homopoly(VBDC)<sup>a</sup>

Time (h)	Total yield (g)	Homo PMMA (g)	Graft copolymer			
			Yield (g)	$\eta_{sp}/C^b$ (dL/g)	[MMA] <sup>c</sup> (mol %)	$T_g$ (°C)
0.5	0.23	0.00	0.09	0.28	53.7	76.2
1.0	0.31	0.00	0.14	0.30	72.2	79.2
1.5	0.40	0.03	0.19	0.43	76.8	86.3
2.0	0.45	0.07	0.24	0.35	82.0	88.0
2.5	0.53	0.33	0.10	0.45	85.3	103.1
3.0	0.59	0.26	0.22	0.52	88.9	100.9

<sup>a</sup> Polymerized in benzene (10 mL) at 30°C, 3 cm from UV source; [VBDC] = [TD] =  $7.6 \times 10^{-2}$  M, [MMA] = 3.77 M TD; tetraethylthiuram disulfide.

<sup>b</sup> In benzene at 30°C; 0.5 g/dL.

<sup>c</sup> Determined by elemental analysis of sulfur.

were obtained in high yields. Otsu et al.<sup>7</sup> graft-copolymerized St or MMA using dithiocarbamate compounds attached to polystyrene gel through a hydrolyzable ester spacer as a polymeric photoiniferter. The yield and  $M_n$  of the side chain homopolymers isolated from the resultant graft copolymers by hydrolysis were found to increase with reaction time. From these results, they concluded that these graft copolymerization proceeded via a living radical mechanism. The present results show that yields of whole polymers increase with irradiation time (Table I). The molecular weights of the resultant graft copolymers, which are estimated from reduced viscosities and the grafted MMA content, increase with the polymerization time. The above results show that these photo graft copolymerizations using homoPVBDC also proceed via a living radical mechanism.

The thermogram of each graft copolymer shows a broader  $T_g$ , which indicates the considerable penetration of MMA chains into PVBDC domains, resulting

TABLE II  
Graft Copolymerization of 4-VPy onto Homopoly(VBDC)<sup>a</sup>

Time (h)	Total yield (g)	Homo PVPy (g)	Graft copolymer			
			Yield (g)	$\eta_{sp}/C^b$ (dL/g)	[VPy] <sup>c</sup> (mol %)	$T_g$ (°C)
0.5	0.40	0.04	0.24	0.42	58.7	84.5, 124.5
1.0	0.67	0.22	0.29	0.45	64.5	93.2, 117.4
1.5	0.86	0.26	0.33	0.62	74.3	114.7
2.0	1.10	0.18	0.37	0.67	77.4	123.2

<sup>a</sup> Polymerized in DMSO (10 mL) at 30°C, 3 cm from UV source [VBDC] = [TD] =  $7.6 \times 10^{-2}$  M, [VPy] = 3.77 M.

<sup>b</sup> In  $\text{CHCl}_3$  at 30°C, 1.0 g/dL.

<sup>c</sup> Determined by elemental analyses of sulfur, nitrogen, and carbon.

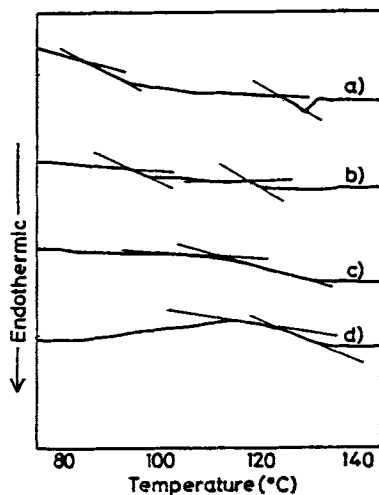


Fig. 2. DSC thermograms of VBDC-*g*-VPy; irradiation time (h): (a) 0.5; (b) 1.0; (c) 1.5; (d) 2.0.

in the more diffuse phase boundaries. The  $T_g$ 's of graft copolymers approach the  $T_g$  of the homoPMMA ( $T_g = 121.6^\circ\text{C}$ ) as polymerization time increases. The graft copolymer which is polymerized for 3 h shows a sharper transition than the others.

### Graft Copolymerization of VPy onto Homo-PVBDC

VPy can also be polymerized using homoPVBDC iniferter under UV irradiation. In this case, polymerizations are carried out in a similar manner as with MMA, and the polymerization tendency is similar to that of MMA (Table II). However, as shown in Fig. 2, the thermograms of 4-VPy grafted copolymers are different from those of MMA grafts. In the initial stages of 4-VPy graft

TABLE III  
Graft Copolymerization of MMA onto Copoly(VBDC-St)<sup>a</sup>

Copoly(VBDC-St)			Total yield (g)	Graft copolymer			
(g)	[VBDC] (mol %)	[St] (mol %)		Yield (g)	$\eta_{sp}/C^b$ (dL/g)	[MMA] <sup>c</sup> (mol %)	$T_g$ ( $^\circ\text{C}$ )
0.20	100.0	0.0	0.40	0.19	0.43	76.8	86.3
0.22	80.0	20.0	0.36	0.10	0.34	73.5	74.3, 110.8
0.26	58.3	41.7	0.44	0.19	0.27	71.4	80.9, 108.0
0.39	29.0	71.0	0.57	0.52	0.26	61.1	76.9, 108.5

<sup>a</sup> Polymerized in benzene (10 mL) at  $30^\circ\text{C}$  for 1.5 h; 3 cm from UV source; [VBDC] = [TD] =  $7.6 \times 10^{-2} M$ , [MMA] =  $3.77 M$ .

<sup>b</sup> In benzene at  $30^\circ\text{C}$ ; 0.5 g/dL.

<sup>c</sup> Determined by elemental analysis of sulfur.

TABLE IV  
Graft Copolymerization of 4-VPy onto Copoly(VBDC-St)(58/42)<sup>a</sup>

Time (h)	Total yield (g)	Homo-PVPy (g)	Graft copolymer			
			Yield (g)	$\eta_{sp}/C^b$ (dL/g)	[VPy] <sup>c</sup> (mol %)	$T_g$ (°C)
0.5	0.57	0.08	0.31	0.44	57.0	93.1, 124.8
1.0	0.88	0.33	0.46	0.46	71.1	105.5, 133.9
1.5	1.11	0.44	0.57	0.70	74.6	101.5, 134.1

<sup>a</sup> Polymerized in DMSO (10 mL) at 30°C, 3 cm from UV source; [VBDC] = [TD] =  $7.6 \times 10^{-2}$  M, [VPy] = 3.77 M used parent copolymer; VBDC/St = 58.3/41.7.

<sup>b</sup> In  $\text{CHCl}_3$  at 30°C; 0.5 g/dL.

<sup>c</sup> Determined by elemental analyses of sulfur, nitrogen, and carbon.

polymerization, the graft copolymer obtained has two sharp  $T_g$ 's (with smaller  $\Delta T_g$ ), but after 2 h the graft copolymer has only one broad  $T_g$  (with larger  $\Delta T_g$ ). The former two  $T_g$ 's are assigned to that of a parent VBDC polymer and a branched VPy polymer, respectively, and the latter  $T_g$  is placed between the above two  $T_g$ 's.

These results suggest that, in the case of MMA, the branched graft chains (PMMA) penetrate considerably into the main chain domains (PVBDC) in the initial stages of the polymerization. On the other hand, in the case of VPy, the compatibility of the graft chains (PVPy) with the main chain polymer (PVBDC) is very poor in the initial stages. As the result, separation of the microphases occurs and two  $T_g$ 's are observed.

### Graft Copolymerization of MMA or VPy onto VBDC-St Copolymer

MMA or VPy is grafted photochemically onto VBDC-St copolymers. Each thermogram of MMA graft copolymer onto VBDC-St copolymer shows two sharp  $T_g$ 's, which are characteristic of the main and the side chains. The com-

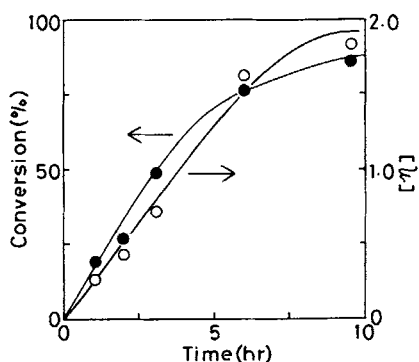


Fig. 3. Photopolymerization of MMA with VBDC as a photoiniferter at 30°C. [MMA] = 9.4 M and [VBDC] =  $1 \times 10^{-3}$  M in bulk;  $[\eta]$  (dL/g).

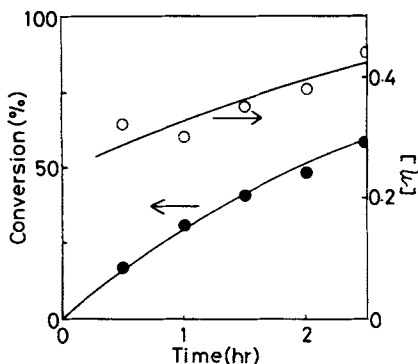


Fig. 4. Photopolymerization of VPy with VBDC as a photoiniferter at 30°C. [VPy] = 3.73 M and [VBDC] =  $1 \times 10^{-2}$  M in DMSO;  $[\eta]$  (dL/g).

position of parent copoly (VBDC-St) does not affect the graft copolymerization (Table III). Graft copolymer of VPy onto copoly (VBDC-St) (58/42) has two  $T_g$ 's even after copolymerization for 1.5 h (Table IV).

#### Photopolymerization of MMA or VPy with VBDC Monomer

The above results show that the different behavior of MMA or VPy in the photo graft copolymerization is due not only to the compatibility of the polymers but also to the mode of a side chain propagation. Therefore, we examined a photopolymerization of MMA or VPy using VBDC monomer, as a photoiniferter (Figs. 3 and 4). In the case of MMA, the yield and  $[\eta]$  of the resultant polymers increase with reaction time. These results suggest that this polymerization may proceed via a living radical mechanism.<sup>1</sup> On the other hand, in the case of VPy, the resultant polymers have a larger value of  $[\eta]$  even at an early stage of polymerization, and the value of  $[\eta]$  does not appreciably increase with photoirradiation time.

These results indicate that the graft copolymerization of MMA proceeds with the consecutive propagation of side chains, and that the graft copolymerization of VPy proceeds with an increase in the number of long side chains. Therefore, the thermograms of MMA graft copolymers show patterns characteristic of homogeneous system, while those of VPy graft copolymers show patterns more characteristic of phase separation. In the graft copolymer of MMA onto VBDC-St copolymer, phase separation, as indicated by  $T_g$ , may occur because the initiating groups are dispersed on the main chain.

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