

## Radical Copolymerization of Ethylene Glycol Bis(Methyl Fumarate) with N-Vinylcarbazole

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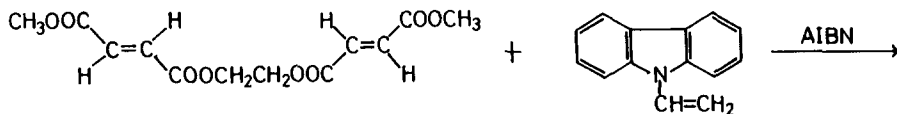
### SUMMARY

For the purpose of elucidating copolymerizability of ethylene glycol bis(methyl fumarate), a new multifunctional monomer, its free-radical copolymerization with N-vinylcarbazole has been studied. The results show that free-radical copolymerization of ethylene glycol bis(methyl fumarate) with N-vinylcarbazole produces soluble copolymers at low conversions, the compositions of which vary from 1:1 to increasingly VCZ rich (below 2.0) with an increase in the VCZ content in the monomer feed. It is suggested that 1:1 alternating copolymerization proceeds and that cyclo-propagation becomes predominant when the monomer feed composition becomes rich in VCZ. Gelation occurs at relatively high conversions.

### INTRODUCTION

Free-radical polymerizations of multifunctional vinyl, allyl, and acrylate monomers are of technological importance for the production of various resins. Polymerization reactions of such multifunctional monomers involve not only usual 1,2- or 1,4-addition propagation but also cyclo-propagation and cross-linking. Therefore, it is of importance to elucidate polymerization behavior of such multifunctional monomers.

In a previous paper some of us have reported the synthesis of a new multifunctional monomer, ethylene glycol bis(methyl fumarate) (EGBMF), and its free-radical homopolymerization (1). In the present study, free-radical copolymerization of EGBMF with N-vinylcarbazole (VCZ) was investigated in order to elucidate copolymerization behavior of EGBMF. The results are compared with our previous results of the copolymerization of diethyl fumarate with VCZ, which produces 1:1 alternating copolymers regardless of the monomer feed composition (2).



## EXPERIMENTAL

Ethylene glycol bis(methyl fumarate) (EGBMF) was prepared by the method described in the previous paper (1), mp 104.5°C. N-Vinylcarbazole (VCZ) (Tokyo Kasei Kogyo Co. Ltd. Japan) was recrystallized twice from methanol, then twice from n-hexane, and dried in vacuo, mp 65°C. 2,2'-Azobisisobutyronitrile (AIBN) (Wako Pure Chemical Industry Ltd. Japan) was purified by recrystallization from methanol. Dioxane was refluxed over sodium wire and distilled in vacuo immediately before use.

Copolymerization was carried out in a dioxane solution by using AIBN as an initiator. The solution containing the monomers and AIBN was introduced into a pyrex glass tube of 20 mm in diameter, evacuated at  $10^{-3}$  torr by several freeze-pump-thaw cycles, and then sealed off. The polymerization solution was placed in a thermostat maintained at  $60 \pm 0.1^\circ\text{C}$ . After polymerization, polymers were precipitated by pouring the polymerization solution into a large amount of chilled diethyl ether and purified by repeated reprecipitation from a tetrahydrofuran (THF) - diethyl ether system to remove the unreacted monomers. Molecular weights of copolymers were determined by means of GPC.

## RESULTS AND DISCUSSION

Free-radical copolymerization of EGBMF with VCZ proceeded to yield copolymers in the form of white powder.

The rate feature of the free-radical copolymerization of EGBMF with VCZ was found to resemble that of the 1:1 alternating radical copolymerization of diethyl fumarate with VCZ. Figure 1 shows the overall initial copolymerization rate as a function of the monomer feed mole ratio. The rate increased almost linearly with an increase in the VCZ content in the monomer feed.

Copolymers obtained at relatively low conversions were soluble in THF, dioxane, and benzene, but insoluble in diethyl ether, n-hexane, and alcohol. But those obtained at relatively high conversions contained insoluble gels.

Soluble copolymers were characterized by IR, UV, and fluorescence spectra, and elemental analysis. The IR absorption spectra of the copolymers show strong bands at  $1720\text{ cm}^{-1}$ , and at  $745$  and  $720\text{ cm}^{-1}$ , which are

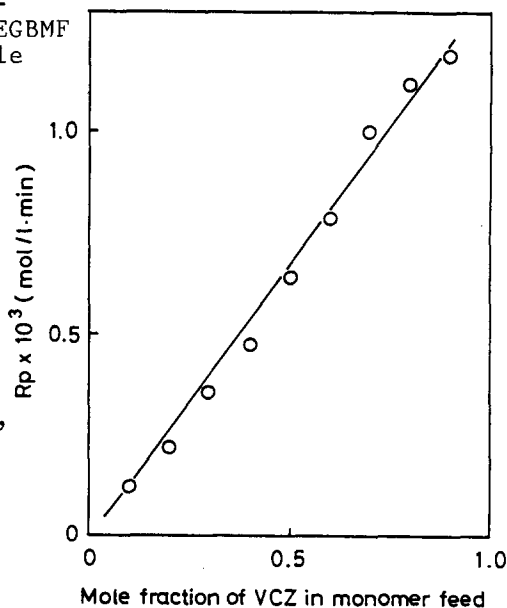


Fig. 1. Initial copolymerization rates as a function of the monomer feed mole ratio.  $[\text{EGBMF}] + [\text{VCZ}] = 1.0\text{ mol dm}^{-3}$ .  $[\text{AIBN}] = 5 \times 10^{-3}\text{ mol dm}^{-3}$ . Temp.:  $60^\circ\text{C}$ ; Solvent: Dioxane.

due to the carbonyl stretching vibration and to the C-H out-of-plane deformation vibration of the carbazole ring, respectively. The IR absorption bands at 960 and 860  $\text{cm}^{-1}$ , which are due to the vinyl group in VCZ, disappeared in the copolymers. Figure 2 shows the electronic absorption and fluorescence spectra of the copolymers. It should be noted that the copolymers produced at various monomer feed mole ratios show the same electronic absorption band position, which is almost the same as that of the 1:1 alternating copolymer of diethyl fumarate with VCZ (2). That is, the copolymers show an absorption band with  $\lambda_{\text{max}}$  at 337.5 and 324 nm arising from the  $\pi-\pi^*$  transition of the carbazole chromophore, which is shifted to the blue region by ca. 6 nm as compared with that of a VCZ homopolymer. Also noteworthy is that the fluorescence spectra of the copolymers exhibit only monomeric fluorescence with no excimer fluorescence, as observed for the 1:1 alternating copolymer of diethyl fumarate with VCZ (2). The results of the electronic absorption and fluorescence emission spectra indicate that the structure of the copolymers of EGBMF with VCZ consists of an alternating arrangement of the VCZ unit and the methyl fumarate moiety.

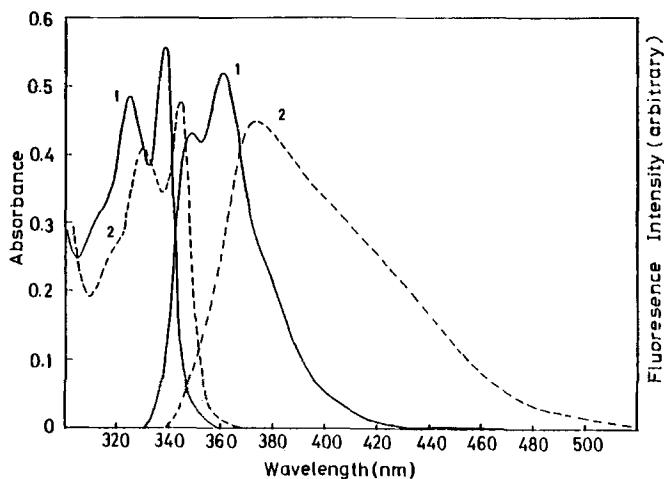


Fig. 2. Electronic absorption and fluorescence spectra of the copolymer of EGBMF with VCZ and a VCZ homopolymer in THF at room temperature. The VCZ homopolymer was prepared by AIBN-initiated free-radical polymerization of VCZ in benzene.  
 1 (—): [copolymer] =  $1.6 \times 10^{-4} \text{ mol dm}^{-3}$   
 2 (---): [VCZ homopolymer] =  $1.3 \times 10^{-4} \text{ mol dm}^{-3}$

Table 1 shows copolymer compositions for various monomer feed mole ratios as determined from carbon and nitrogen analyses of copolymers obtained at low conversions, i.e., less than 10%. Number-average molecular weights of these copolymers as determined by GPC using polystyrene as a standard sample are also listed. The results show that compositions of the copolymers vary from 1:1 to increasingly VCZ rich (below 2.0) with an increase in the VCZ content in the monomer feed.

Table 1. Compositions and number-average molecular weights of copolymers obtained at various monomer feed ratios.

Mol Fraction of VCZ In Monomer Feed	N (%)	C (%)	Mol Fraction of VCZ In Copolymer		$\bar{M}_n$
			from N (%)	from C (%)	
0.1	2.82	63.47	0.49	0.45	—
0.2	2.97	65.50	0.50	0.51	9000
0.3	3.15	66.18	0.53	0.53	10000
0.4	3.15	66.66	0.53	0.54	15000
0.5	3.27	67.13	0.55	0.55	16000
0.6	3.35	67.47	0.56	0.57	17000
0.7	3.45	68.09	0.57	0.58	25000
0.8	3.55	68.29	0.59	0.59	37000
0.9	3.78	69.30	0.62	0.61	51000

The copolymer composition data shown in Table 1, however, do not mean that the copolymers with compositions rich in VCZ have a VCZ - VCZ sequence. Instead, it is indicated from the results of the electronic absorption and fluorescence emission spectra that the structure of the copolymers consists of an alternating arrangement of the VCZ unit and the methyl fumarate moiety. This is supported from the results obtained for copolymers of diethyl maleate with VCZ. Unlike the 1:1 alternating copolymer of diethyl fumarate with VCZ, the copolymers of diethyl maleate with VCZ have compositions which vary from 1:1 to increasingly VCZ rich with an increase in the VCZ content in the monomer feed. The electronic absorption band position of the copolymers of diethyl maleate with VCZ varies depending on the composition, and the copolymers with compositions rich in a VCZ content exhibit excimer fluorescence arising from the presence of a VCZ - VCZ sequence, its intensity increasing with an increase in the VCZ content (3, 4). It is suggested that in the present copolymerization system 1:1 alternating propagation proceeds and that cyclo-propagation becomes predominant at low EGBMF feed ratios, that is, a propagating VCZ end tends to attack intramolecularly the penultimate methyl fumarate double bond in a growing polymer to yield copolymers rich in the VCZ content. It is assumed that the copolymers with compositions rich in VCZ should have less content of the pendant double bond relative to the copolymers with the 1:1 composition. An attempt to quantify the content of the pendant double bond in each copolymer by means of  $^1\text{H}$  NMR spectra was unsuccessful because of the overlap of the signals of the olefinic protons with those of the carbazole ring protons. However, the IR absorption spectra of the copolymers taken both for KBr disks and for chloroform solutions of the same concentration show that the relative intensity of the band arising from the trans =C-H out-of-plane deformation vibration at  $980\text{ cm}^{-1}$  to that arising from the carbonyl stretching vibration at  $1730\text{ cm}^{-1}$  is weaker for the copolymers with higher VCZ

contents than for the copolymers with the 1:1 composition: for example, the intensity for the copolymer with the VCZ mole fraction of 0.61 is about a half of that for the copolymer with the VCZ mole fraction of 0.51 (Figure 3). Thus the copolymers with the 1:1 composition are 1:1 alternating copolymers of EGBMF with VCZ, and the copolymers with compositions rich in the VCZ content have the following general structure, which consists of alternating arrangements of the VCZ unit and the methyl fumarate moiety as a result of cyclo-propagation.

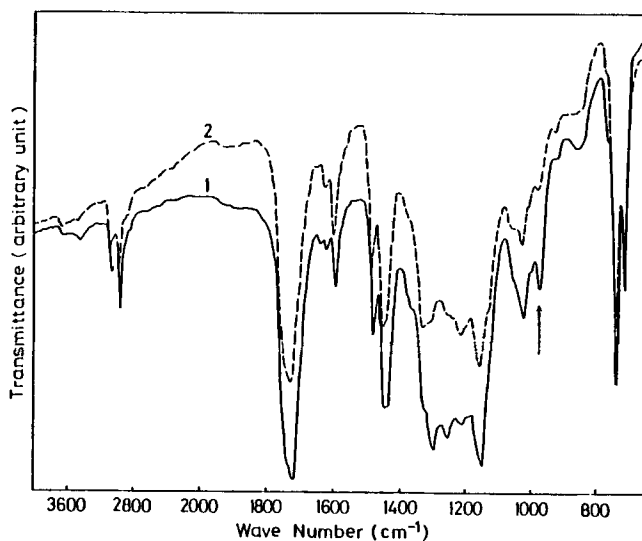
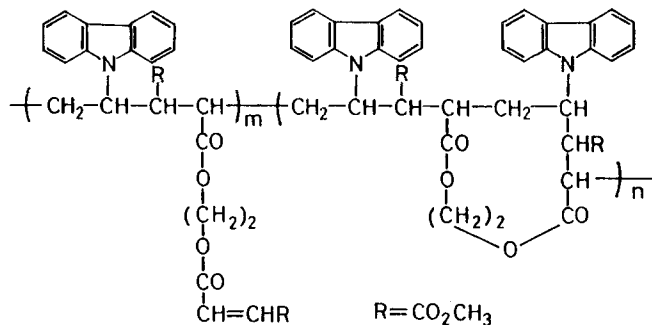


Fig. 3. Infrared absorption spectra of copolymers of EGBMF with VCZ taken for KBr disks. 1 (—) and 2 (----): copolymers with VCZ mole fractions of 0.51 and 0.61, respectively.

Cross-linking reactions occurred with increasing conversions. Figure 4 shows GPC curves for copolymers obtained at different conversions. As seen in the Figure, the molecular-weight distribution of soluble copolymers broadens with increasing conversions as a result of the occurrence of cross-linking reactions.

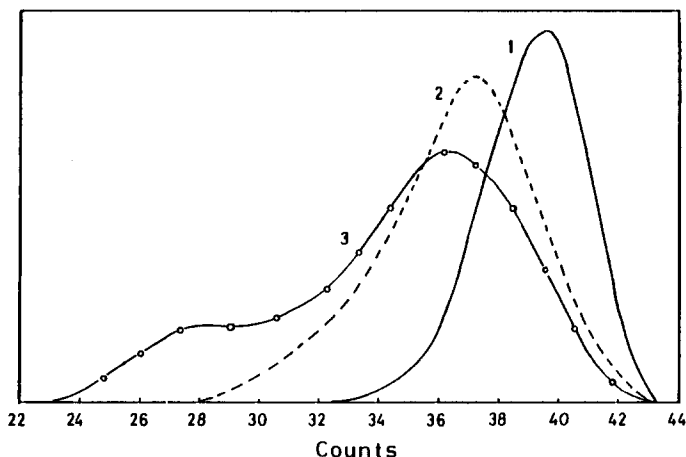


Fig. 4. GPC curves for copolymers obtained at different conversions.  $[EGBMF] = [VCZ] = 0.5 \text{ mol dm}^{-3}$ ;  $[AIBN] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; polym. temp.,  $60^\circ\text{C}$ ; solvent, dioxane. 1: 1.6%, 2: 4.2%, 3: 8.8% conversions.

Figure 5 shows time - conversion plots for the formation of total polymers and gels, respectively, in the free-radical copolymerization of EGBMF with VCZ at a monomer feed mole ratio of 1:1. The result shows that gelation occurs at about 10% conversion under this condition.

In summary, free-radical copolymerization of EGBMF with VCZ produces soluble copolymers at low conversions, the compositions of which vary from 1:1 to increasingly VCZ rich (below 2.0) with an increase in the VCZ content in the monomer feed. The spectral data indicate that the structure of the copolymers consists of alternating arrangements of the VCZ unit and the methyl fumarate moiety. In the free-radical copolymerization of EGBMF with VCZ, 1:1 alternating propagation proceeds and cyclo-propagation accompanies at low EGBMF feed ratios, resulting in the formation of copolymers with compositions rich in VCZ. Gelation occurs at relatively high conversions, e.g., about 10% conversion at a monomer feed mole ratio of 1:1.

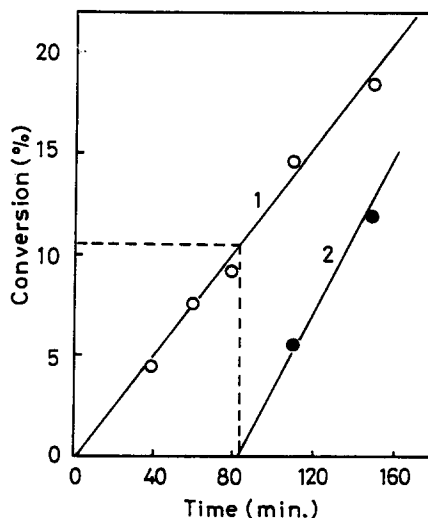


Fig. 5. Time - polymer yield plots for the free-radical copolymerization of EGBMF with VCZ under the condition described in Fig. 4. 1 (O): total polymers; 2 (●): gels.

Since 1:1 alternating copolymers produced in the free-radical copolymerization of EGBMF with VCZ have olefinic double bonds as pendant groups, it is expected that they undergo cross-linking reactions by irradiation of electron beam or uv light in the presence of photo-initiators, and hence they may function as materials for use in relief image formation.

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