

Copolymerization of 1,1-Diphenylethylene with *m*- and *p*-Divinylbenzenes and Grafting Reaction of the Resulting Copolymer with Methacrylates

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Summary

Copolymerizations of 1,1-diphenylethylene (DPE) with *m*- or *p*-divinylbenzene (DVB) were carried out in THF and toluene using alkylolithiums as initiators, and the monomer reactivity ratios were determined. The copolymers prepared in the presence of excess DPE over DVB had a highly alternating character and was harder to form a crosslinked polymer as compared with the homopolymer of DVB. The copolymer was treated with $\text{sec-C}_4\text{H}_9\text{Li}$ in THF, and the resulting polyanion was reacted with several methacrylates to form the graft copolymers with polymethacrylate branches.

Introduction

1,1-Diphenylethylene (DPE) can not be polymerized to high molecular weight polymer with any initiators owing to the steric hindrance due to the phenyl substituents (EVANS and GEORGE 1961, EVANS and GEORGE 1962). However, it can copolymerize with styrene (YUKI et al., 1964, YUKI et al., 1967), substituted styrene (YUKI and OKAMOTO 1970a), conjugated dienes (YUKI et al., 1964, YUKI and OKAMOTO 1970b, YUKI and OKAMOTO 1969a, YUKI et al., 1968, YUKI et al., 1969b) in the presence of anionic initiators, and form alternating copolymers under certain conditions.

In this work DPE was copolymerized with *m*- and *p*-divinylbenzenes (*m*-DVB and *p*-DVB) mostly in tetrahydrofuran (THF) using alkylolithiums as initiators and the monomer reactivity ratios were determined for the copolymerizations. The resulting copolymers have the pendant vinyl groups and can be used as starting materials for various functional polymers and graft copolymers.

The copolymers prepared in the presence of excess DPE over DVB had a highly alternating character, and was harder to form a gel and easier to handle as compared with the homopolymer of *m*- or *p*-DVB since most of the DVB units in the copolymer were flanked with DPE units on both sides. The copolymer was converted into the polyanion by the reaction with $\text{sec-C}_4\text{H}_9\text{Li}$ in

THF and the resulting polyanion was reacted with various methacrylates to form the graft copolymer with poly-methacrylate branches. The results are also described briefly.

Experimental

DPE was prepared by the dehydration of 1,1-diphenylethanol, which was obtained from phenylmagnesium bromide and acetophenone (KAUFFMANN 1906). The DPE was treated with C_4H_9Li to remove a small amount of contaminants and distilled under reduced nitrogen pressure just before use.

p-DVB and m-DVB were kindly supplied by Asahi Chemical Co., and dried over calcium dihydride and distilled under high vacuum. The purities from GLPC analysis were as follows:

p-DVB: p-isomer 96.0, m-isomer 3.5, ethylvinylbenzene 0.5%

m-DVB: p-isomer 5.1, m-isomer 93.4, ethylvinylbenzene 1.5%.

Toluene and THF were purified by ordinary method, and dried by the addition of the solution of C_4H_9Li in toluene and $LiAlH_4$, respectively. The dried solvents were vacuum-distilled just before use.

C_2H_5Li , C_2D_5Li , C_4H_9Li and sec- C_4H_9Li were synthesized from the corresponding alkyl chloride and metallic lithium in heptane (ZIEGLER and COLONIUS 1930) and the concentrations of the solutions were determined by the titration with sec-butyl alcohol using 2,2'-biquinoline as an indicator (WATSON and EASTHAM 1967, ELLISON et al., 1972).

Copolymerization and graft polymerization reactions were carried out in a glass ampoule under dry nitrogen. Nitrogen gas was dried by passing through the column packed with molecular sieves 4A cooled at $-78^\circ C$. The polymerization reaction was terminated by adding a small amount of methanol and the reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by filtration, washed several times with methanol and dried under vacuum.

The 1H NMR spectra of polymer were measured in chloroform-d at $60^\circ C$ on a JEOL JNM-MH-100 (CW) or a JEOL JNM-FX100 (FT) spectrometer.

The number-average molecular weight of the polymer was measured on a Hitachi 117 vapor pressure osmometer in toluene at $60^\circ C$. The molecular weight distribution was determined with a JASCO FLC-A10 GPC chromatograph with Shodex GPC column A-80M ($50cm \times 2$) with maximum porosity of 5×10^7 using THF as a solvent. The chromatogram was calibrated against standard polystyrene samples.

Results and Discussion

Copolymerizations of DPE and m-DVB were carried out with C_2H_5Li and C_2D_5Li in THF at $-78^\circ C$ and at the initial monomer ratio of m-DVB/DPE = 0.5. The results

are shown in Table 1. The soluble homopolymer of m-DVB or p-DVB, which was prepared in THF with C₄H₉Li at -78°C, showed a strong exothermic peak at about 160°C in DSC thermogram (HATADA et al., unpublished) but the copolymer products obtained here did not show any detectable signal around this temperature. This indicates that the products are really the poly(DPE-co-m-DVB) and do not contain the homopolymer of m-DVB.

Table 1
Copolymerization of DPE(M₁) and m-DVB(M₂) in THF
with alkylolithiums at -78°C^a

Initiator (mmol)	Total monomer (mmol)	THF (ml)	Time (hr)	Yield ^b (%)	Polymer				
					M ₂ ^c M ₁	M _n		CHE ^e	
					VPO	Calc. ^d			
C ₂ H ₅ Li	0.08	30	25	6	6.0	1.38	3,300	3,690	0.99
C ₂ D ₅ Li	0.08	30	25	6	5.6	1.39	3,400	3,390	1.04
C ₄ H ₉ Li ^f	0.09	90	75	24	52.4	1.19	74,000 ^g	82,300	—

^a Initial monomer ratio m-DVB/DPE = 0.5 mol/mol.

^b Percentage based on the weight of the total monomer charged.

^c Molar ratio determined by ¹H NMR spectra.

^d Calculated from the amount and composition of the copolymer and the amount of the initiator used.

^e Number of terminal methine proton per polymer molecule.

^f Polymerization at -20°C.

^g Determined by GPC.

¹H NMR spectra of the copolymer formed are given in Figure 1. The assignment of the peaks is indicated in the Figure. In the spectrum of the low molecular weight copolymer prepared with C₂H₅Li (Figure 1A) there appears the resonance at 0 ~ 1 ppm due to the initiator fragments (C₂H₅-), which were introduced into the copolymer molecule through the initiation reaction. The resonance overlaps with that of the backbone methylene protons, but the intensity can be estimated by the comparison of the spectrum with that of the polymer prepared with C₂D₅Li (Figure 1B). This led to the accurate determination of the composition of low molecular weight copolymer. The copolymer of high molecular weight prepared with C₄H₉Li did not show any detectable signal due to the initiator fragments as shown in Figure 1C.

A small peak at 3.0 ppm in Figure 1A or Figure 1B was assigned to the terminal methine proton ($\sim\text{CH}_2-\overset{\text{Ph}}{\underset{\text{Ph}}{\text{C}}}-\text{H}$)

since it disappeared when the reaction was terminated by deuterated methanol and the chemical shift was close to that of the methine proton of 1,1-diphenylhexane (2.9 ppm). The intensity of the signal was one fifth of the intensity of the signal due to the initiator fragment in Figure 1A. The number of the methine proton in a copolymer molecule was calculated to be about unity from the measurements of NMR signal intensity and the molecular weight. The molecular weights of the

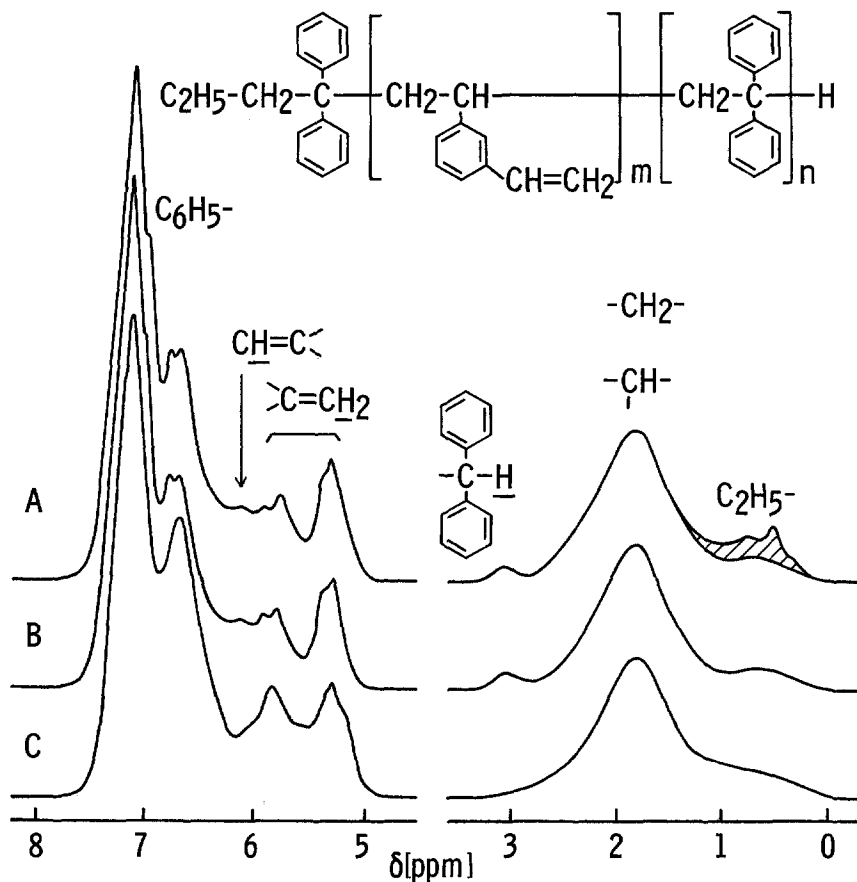


Figure 1 100MHz ^1H NMR spectra measured in CDCl_3 at 60°C of the copolymers of DPE and *m*-DVB prepared in THF by (A) $\text{C}_2\text{H}_5\text{Li}$, (B) $\text{C}_2\text{D}_5\text{Li}$ and (C) $\text{C}_4\text{H}_9\text{Li}$

copolymers measured by vapor pressure osmometer were in agreement with those calculated from the yield and composition of the copolymer and the initiator concentration (Table 1). These results indicate that the copolymer obtained has a linear structure and the attack of the propagating anion onto the pendant vinyl bond hardly occurred during the reaction.

Copolymerizations of DPE with *m*-DVB and *p*-DVB were carried out in THF with $\text{C}_4\text{H}_9\text{Li}$ at -78°C . The results are given in Tables 2 and 3. The apparent rate of copolymerization decreased with a decrease in the initial concentration of DVB. This should be due to the smaller rate constant for the addition of DPE anion to DVB compared with that for the DVB anion to DPE. Similar situation was found in the anionic copolymerization of DPE and styrene in THF (URETA et al., 1966,

YUKI et al., 1967). The copolymer prepared at the initial monomer ratio (DVB/DPE) lower than 0.33 contained a small amount of chloroform-insoluble fraction. The polymer prepared in the copolymerization at p-DVB/DPE of 0.05 for 24hr was mostly insoluble in usual organic solvents. Attack of the DPE anion at the propagating end on the pendant vinyl group of the polymer chain may occur at low concentration of DVB.

Table 2
Copolymerization of DPE(M₁) and m-DVB(M₂) in THF with C₄H₉Li at -78°C and various monomer ratios^a

Monomer M ₂ /M ₁ (mol/mol)	C ₄ H ₉ Li (mmol)	Time (hr)	Polymer	
			Yield (%)	M ₂ /M ₁ (mol/mol)
∞ ^b	0.10	20sec	80.1	—
2.00 ^c	0.02	7	4.7	2.76
0.96	0.09	0.33	0.3	2.10
0.51	0.08	6	5.3	1.67
0.33	0.07	19	5.1	1.26
0.19	0.06	24	2.8	1.20

^a Total monomer 30mmol, THF 25ml.

^b Homopolymerization, m-DVB 10mmol.

^c Total monomer 15 mmol.

Table 3
Copolymerization of DPE(M₁) and p-DVB(M₃) in THF with C₄H₉Li at -78°C and various monomer ratios^a

Monomer M ₃ /M ₁ (mol/mol)	C ₄ H ₉ Li (mmol)	Time (min)	Polymer	
			Yield (%)	M ₃ /M ₁ (mol/mol)
∞ ^b	0.10	20sec	97.1	—
2.75 ^c	0.02	2	6.7	8.80
0.93	0.09	2	9.8	3.24
0.46	0.08	2	1.2	2.51
0.33	0.07	12	5.4	2.11
0.18	0.06	20	3.4	1.23
0.05	0.05	24hr	6.5 ^d	—

^a Total monomer 30mmol, THF 25ml.

^b Homopolymerization, p-DVB 10mmol.

^c Total monomer 10mmol.

^d The copolymer was mostly insoluble in usual organic solvents.

The monomer reactivity ratios for the copolymerizations of DPE(M₁) with m-DVB(M₂) and p-DVB(M₃) were calculated from the data in Tables 2 and 3, and the results are shown in Table 4. The rate constant for the addition of nucleophilic reagent toward p-DVB is larger than that for m-DVB (YUKAWA et al., 1979), indicating the higher reactivity of p-DVB. Actually, the rate of homopolymerization of p-DVB is larger than that of m-DVB as shown in Tables 2 and 3, that is, $k_{33} > k_{22}$. On the other hand, the reactivity of p-DVB anion may be slightly lower than that of m-DVB anion owing to a

larger resonance stabilization of the former anion. This is the reason why r_3 is larger than r_2 . The monomer reactivity ratios were little affected by the reaction temperature (Table 4), although the apparent rate of copolymerization increased with an increase in the temperature.

Table 4
Monomer reactivity ratios for the copolymerization
of DPE(M_1) with m-DVB(M_2) and p-DVB(M_3)

Solvent	Temp. (°C)	r_1	$r_2(=k_{22}/k_{21})$	$r_3(=k_{33}/k_{31})$
THF	-78	0.0	1.2	—
THF	-78	0.0	—	2.8
THF	-20	0.0	1.2	—
THF	-20	0.0	—	2.5
Toluene	-20	0.0	2.5	—
Toluene	-20	0.0	—	16

The copolymerization did not occur in toluene at -78°C , but appreciably occurred at -20°C . The values of r_2 and r_3 for the copolymerization in toluene at -20°C were larger than those in THF. This may be due to the structural difference of the propagating chain ends in both solvents, although the true mechanism is not clear at present. The same phenomenon was observed in the anionic copolymerization of DPE and styrene at 30°C (YUKI et al., 1967).

Grafting reactions of methyl methacrylate with the alternating copolymer of DPE and m-DVB were carried out in THF at -78°C by using $\text{sec-C}_4\text{H}_9\text{Li}$. The copolymer (m-DVB/DPE = 1.19 mol/mol, $M_n = 74,000$, cf. Table 1) was reacted with $\text{sec-C}_4\text{H}_9\text{Li}$ equimolar to the amount of pendant vinyl group in THF at -78°C for 1 hr, and the polyanion formed was partially killed by adding the 80% molar amount of methanol. MMA monomer was then vacuum-distilled into the solution of the resulting anion, and grafted. The deep red color of the anion was disappeared upon the addition of MMA. The graft copolymer (Table 5, No. 1) formed was completely insoluble in acetonitrile, which dissolves the homopolymer of MMA. The GPC curve of the graft copolymer shifted to the high molecular side as compared with that of the original alternating copolymer and did not show the peak ascribed to the latter polymer. The results indicate that the graft copolymer obtained hardly contain the original copolymer as well as the homopolymer of MMA.

When a large amount of MMA was grafted (Table 5, No. 2), the resulting graft copolymer could be dissolved in acetonitrile at 60°C . However, the ^1H NMR spectrum of the polymer in acetonitrile- d_3 measured at 60°C showed much broader signals as compared with the spectrum measured in chloroform- d . This suggests that the graft copolymer is forced to be solubilized in aceto-

Table 5
Grafting reaction of methacrylate with poly(DPE-co-m-DVB)
in THF at $-78^{\circ}\text{C}^{\text{a}}$

No.	Backbone copolymer (mg)	Methacrylate		Time (hr)	Yield (mg)	Graft copolymer		
		Ester group	(mmol)			Grafted methacrylate (%)	$M_n \times 10^{-3}$	
						GPC	Calcd ^b	
1	212	CH ₃	2.83	1	440	66	162	155
2	201	CH ₃	18.8	12	2061 ^c	97	389	729
3	220	CH ₃ ^d	2.83	0.33	377 ^e	26	—	—
4	220	C ₂ H ₅	2.40	6	426	63	133	146
5	205	t-C ₄ H ₉	1.76	12	482	95	124	173
6	201	t-C ₄ H ₉ ^d	1.76	12	368	51	98	136

^a THF 60ml.

^b Calculated from the amount and molecular weight of the original copolymer and the amount of methacrylate monomer grafted.

^c The graft copolymer obtained was soluble in acetonitrile at 60°C .

^d The grafting reaction was carried out without partially killing the polyanion.

^e The graft copolymer obtained was insoluble in usual organic solvents.

nitride owing to the long branches of PMMA, which is soluble in this solvent. The reason for the large difference between the observed and calculated molecular weights is now under investigation.

If MMA monomer was added to the polyanion solution without partially killing the anion, the graft copolymer formed was not soluble in any organic solvents (Table 5, No. 3). This may be due to the crosslinking through the attack of the PMMA anion at the carbonyl group in the PMMA branches since the graft copolymer prepared under the similar conditions using *t*-butyl methacrylate (Table 5, No. 6) is completely soluble in chloroform and THF. Carbonyl attack by the initiator occurs more largely in the polymerization with C₄H₉Li of MMA than in that of *t*-butyl methacrylate (HATADA et al., 1979, HATADA et al., 1982). However, the possibility of crosslinking by the association of the polymer molecules through the complex formation among the PMMA branches can not be eliminated.

The graft copolymers of various polymethacrylate branches were prepared in a similar manner. Some of the results are shown in Table 5. The NMR and GPC analyses indicated the formation of graft copolymer. The molecular weights of the graft copolymers determined by GPC were roughly in agreement with those calculated from the molecular weight of the original polymer and the amounts of the original polymer and the grafted methacrylate monomer.

The grafting reaction of poly(DPE-co-DVB) with vinyl and diene monomers are now extensively studied by using various kinds of initiators and the results will be published in near future.

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References

- ELLISON, R. A., GRIFFIN, R., and KOTSONIS, F. N., J. Organometal. Chem., 36, 209 (1972).
- EVANS, A. G. and GEORGE, D. B., J. Chem. Soc., 1961, 4653.
- EVANS, A. G. and GEORGE, D. B., J. Chem. Soc., 1962, 141.
- KAUFFMANN, H., Z. Phys. Chem., 55, 547 (1906).
- HATADA, K., KITAYAMA, T., SUGINO, H., UMEMURA, Y., FUROMOTO, M., and YUKI, H., Polymer J., 11, 989 (1979).
- HATADA, K., KITAYAMA, T., OKAHATA, S., and YUKI, H., Polymer J., 14, 971 (1982).
- HATADA, K., OKAMOTO, Y., KITAYAMA, T., and SASAKI, S., unpublished data.
- URETA, E., SMID, J., and SZWARC, M., J. Polym. Sci., A-1, 4, 2219 (1966).
- WATSON, S. C. and EASTHAM, J. F., J. Organometal. Chem., 9, 165 (1967).
- YUKAWA, J., KATAOKA, K., NITADORI, Y., and TSURUTA, T., Polymer J., 11, 163 (1979).
- YUKI, H., KOSAI, K., MURAHASHI, S., and HOTTA, J., J. Polym. Sci., B2, 1121 (1964).
- YUKI H., HOTTA, J., OKAMOTO, Y., and MURAHASHI, S., Bull. Chem. Soc. Japan, 40, 2659 (1967).
- YUKI H., HATADA, K., and INOUE, T., J. Polym. Sci., A-1, 6, 3333 (1968).
- YUKI, H. and OKAMOTO, Y., Bull. Chem. Soc. Japan, 42, 1644 (1969a).
- YUKI, H., OKAMOTO, Y., and SADAMOTO, K., Bull. Chem. Soc. Japan, 42, 1754 (1969b).
- YUKI, H. and OKAMOTO, Y., Polymer J., 1, 13 (1970a).
- YUKI, H. and OKAMOTO, Y., Bull. Chem. Soc. Japan, 43, 145 (1970b).
- ZIEGLER, K. and COLONIUS, A., Ann., 479, 135 (1930).

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