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## Substituent Effects on Radical Polymerization Behavior of 2,2-(4,4′-Disubstituted-diphenyl)-4-methylene-1,3-dioxolanes

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ABSTRACT: 2,2-(4,4′-Dimethoxydiphenyl)-4-methylene-1,3-dioxolane (**5**), 2,2-(4,4′-dimethyldiphenyl)-4-methylene-1,3-dioxolane (**6**), 2,2-diphenyl-4-methylene-1,3-dioxolane (**7**), 2,2-(4,4′-dichlorodiphenyl)-4-methylene-1,3-dioxolane (**8**), and 2,2-(4,4′-dicyanodiphenyl)-4-methylene-1,3-dioxolane (**9**) were synthesized and polymerized using radical initiators at 60 and 120 °C to undergo predominantly ring-opening accompanying elimination of the corresponding 4,4′-disubstituted benzophenones. It was found that the polymer yields decreased as electron-withdrawing character of the substituents increased. The substituent effects on the polymer yields were discussed in terms of $E_{LUMO}$ (eigenvalue of the lowest unoccupied molecular orbital) and $E_{HOMO}$ (eigenvalue of the highest occupied molecular orbital) of the monomer and $E_{SOMO}$ (eigenvalue of the singly occupied molecular orbital) of the radical.

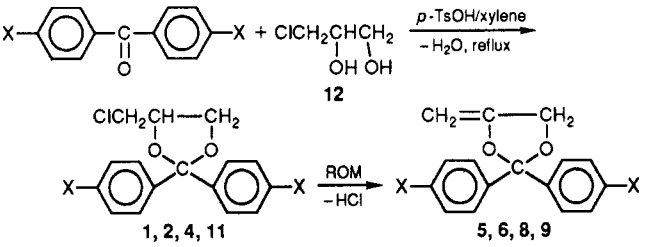
### Introduction

We have previously reported that 2,2-diphenyl-4-methylene-1,3-dioxolane (**7**) undergoes quantitative ring-opening reaction accompanying the elimination of benzophenone to obtain polyketone.[1] In this paper we report the preparation and polymerization of 2,2-(4,4′-disubstituted-diphenyl)-4-methylene-1,3-dioxolanes having para substituents (**5**, $CH_3O$; **6**, $CH_3$; **8**, Cl; **9**, CN) on the phenyl group and estimate their radical polymerizations. It has been already reported that para-substituted styrenes with more electron-withdrawing substituents show a greater overall rate in the radical polymerization due to the interaction between the singly occupied molecular orbital (SOMO) of the radical and the lowest unoccupied molecular orbital (LUMO) of the monomer.[2] On the other hand, Imoto et al. have reported recently that the activation energy ($E_p^*$) of propagation in radical polymerization decreases as the charge transfer from the radical to the monomer in the transition state increases due to the dominant interaction between the SOMO of the radical and the highest molecular orbital (HOMO) of the monomer, and $E_p^*$ is expressed as

$$E_p^* = a - b|E_{SOMO} - E_{LUMO}| \quad (1)$$

where $a$ and $b$ are constants, $E_{SOMO}$ is the eigenvalue of SOMO of the radical, and $E_{LUMO}$ is the eigenvalue of LUMO of the monomer.[3] We discuss the substituent effects on the polymerization in terms of HOMO and the LUMO of the monomers and SOMO of the radical.

**Scheme I**[a]




[a] 1, 5, X = OMe; 2, 6, X = Me; 4, 8, X = Cl; 11, 9, X = CN.

### Results and Discussion

Monomers (**5–9**) were synthesized by acetalization of the corresponding 4,4′-disubstituted benzophenones with 3-chloro-1,2-propanediol, followed by dehydrochlorination with alcoholate to obtain **5–9** as shown in Scheme I. The results are indicated in Tables I and II.

The polymerization of **5–9** was carried out in bulk or benzene using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator at 60 °C and in bulk or chlorobenzene using di-*tert*-butyl peroxide (DTBP) as the initiator at 120 °C. After purification of the obtained polymers, the corresponding substituted benzophenones and unreacted monomer were recovered from the soluble parts in ether without the corresponding oligomers. All the obtained polymers were insoluble in common organic solvents but soluble in hot dimethyl sulfoxide (DMSO) and *m*- or *p*-cresol. All the IR spectra of the polymers showed the absorp-

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**Table I**
**Syntheses of 1, 2, 4, and 11[a]**

| no. | X | p-TsOH, mol % | yield, % |
|---|---|---|---|
| 1 | OMe | 0.9 | 73[b] |
| 2 | Me | 0.9 | 62[b] |
| 4 | Cl | 0.9 | 54[b] |
| 11 | CN | 10 | |

[a] Solvent: xylene. Time: 9 h. [b] Purified by column chromatography, oil.

**Table II**
**Syntheses of 5, 6, 8, and 9[a]**

| no. | X | alcoholate (2 equiv) | yield, % |
|---|---|---|---|
| 5 | OMe | t-BuOK | 93[b] |
| 6 | Me | t-BuOK | 96[b,c] |
| 8 | Cl | MeONa | 65[d] |
| 9 | CN | t-BuOK | 45[b,e] |

[a] Temp: rt. Time: 6 h. [b] Purified by column chromatography. [c] Oil. [d] Bp 120 °C (0.05 mmHg). [e] Mp 127.0–128.0 °C.

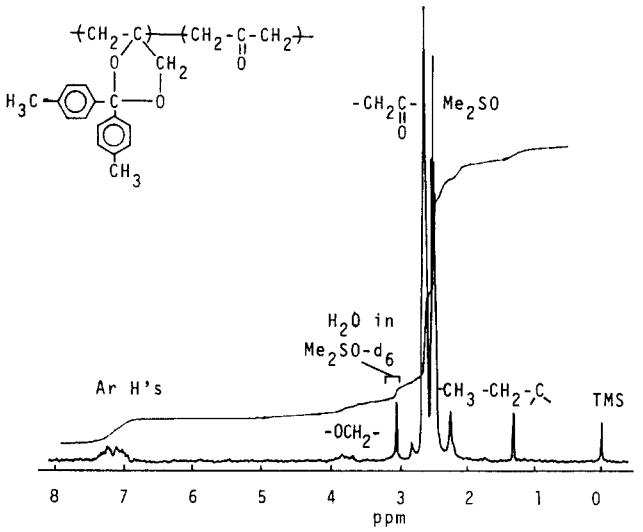
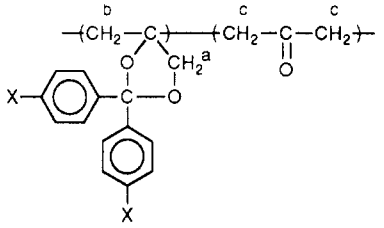



**Figure 1.** $^1$H NMR spectrum (100 MHz, δ, $Me_2SO$-$d_6$, $Me_4Si$) of the polymer obtained from **6** at 60 °C in bulk.

tion around 1700 cm$^{-1}$ assigned to ketone group. $^1$H NMR spectrum of the polymer obtained from **6** at 60 °C in bulk as a representative case was shown in Figure 1. $^1$H NMR data of the polymers obtained from **5–8** at 60 °C in bulk and from **9** in chlorobenzene are listed in Table III. Similar tendency in $^1$H NMR spectra of the polymers formed under different conditions regardless of the substituents observed, but $^1$H NMR spectrum of the polymer obtained from **7** at 120 °C in chlorobenzene showed only one peak at 2.62 ppm as described previously.[1] The peaks at 7.6–6.9, 4.1–3.7, and 1.5–1.1 ppm are assigned to aromatic protons, methylene protons (>C(O–)$OCH_2$–), and methylene protons (–$CH_2$C<), respectively, which can be explained only by assuming that the monomers undergo vinyl polymerization (Scheme II, path A). The peak at 2.6 ppm assigned to methylene protons (–$CH_2$CO–) in the $^1$H NMR spectra, the absorption of ketone group in the IR spectra, and the detection of benzophenones demonstrated that **5–9** underwent the ring-opening polymerization accompanying the elimination of benzophenones during the polymerizations as shown in Scheme II, path B.

The results of the polymerizations are summarized in Table IV. The polymerization of **7** at 120 °C in chlorobenzene was tried again, and the polymer yield was found to be up to 90% without stopping the propagation described previously.[1] It was found that the molar

**Table III**
**$^1$H NMR Data ($Me_2SO$-$d_6$, 100 MHz) of the Polymers Obtained from 5–8 at 60 °C in Bulk and from 9 at 120 °C in Chlorobenzene**



| | δ | | | | |
|---|---|---|---|---|---|
| X | a | b | c | Ar H's | |
| $OCH_3$[a] | 3.61–3.94 | 1.21–1.40 | 2.61 | 6.80–7.40 | 3.72 ($OCH_3$) |
| $CH_3$[a] | 3.71–4.06 | 1.32 | 2.61 | 6.89–7.41 | 2.25 ($CH_3$) |
| H[b] | 3.66–4.08 | 1.14–1.46 | 2.61 | 6.94–7.41 | |
| Cl[a] | 3.80–4.00 | 1.32 | 2.61 | 7.10–7.51 | |
| CN[c] | 3.71–4.14 | 1.07–1.86 | 2.62 | 6.97–7.48 | |

[a] Measured at 80 °C. [b] Measured at 70 °C. [c] Measured at 120 °C.

ratio of unit II in the polymers increased as the polymerization temperature raised and monomers were diluted, because the ring-opening reaction was accelerated with a rise in the temperature. Polymerization in diluted concentration underwent the intramolecular ring-opening reaction in preference to the intermolecular vinyl polymerization. Especially, when the polymerization was carried out at 120 °C in chlorobenzene, unit II was obtained predominantly. It is noteworthy that the substituents scarcely affect the change of polymer composition but the polymer yields decrease as electron-withdrawing character of the substituents increases. From the substituent effect on the polymer yield, the rate-determining step in the polymerization might speculatively be an addition of polymer radical (~$CH_2COCH_2$) to the C=C double bond of the monomers.

The chemical shift of $CH_2$=C< in $^{13}$C NMR spectra of the monomers was plotted as a function of the corresponding Hammett constants to estimate the substituent effect on π-bond of $CH_2$=C< in Figure 2 to observe a linear relationship between the chemical shifts and the σ-values.

The polymer yield might be regarded as the polymerization rate, because all the soluble parts in ether did not contain oligomers. The linear relationship between the polymer yields (60 °C) and the corresponding σ-values (Figure 3) by the Hammett equation (eq 2)

$$\log (Y_X/Y_H) = \rho\sigma \qquad (2)$$

where $Y_X$ is polymer yield from **5**, **6**, **8**, and **9** and $Y_H$ is polymer yield from **7**. The value of ρ was −4.2 in bulk and −1.4 in benzene.

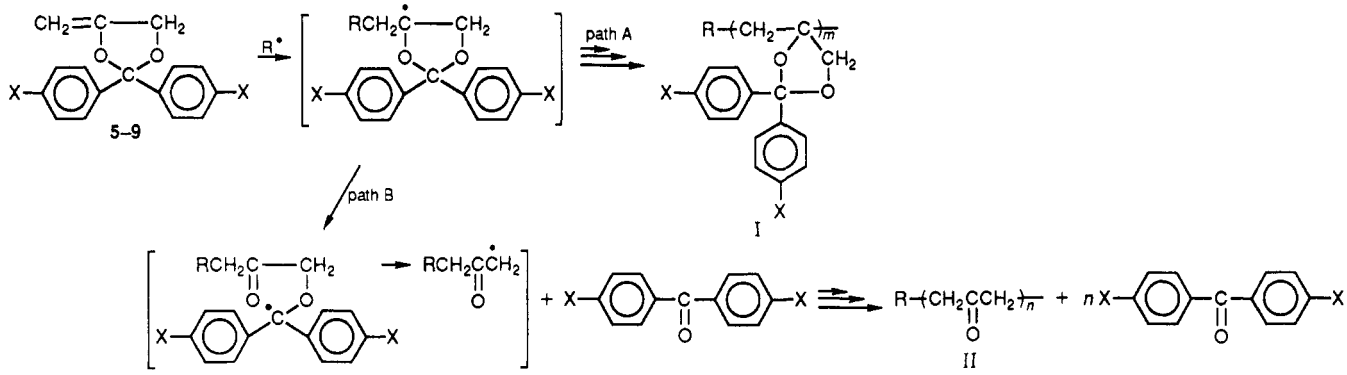
O. H. Rousseau et al. have reported that the eigenvalues of the HOMO and LUMO of monosubstituted benzenes are lowered as the corresponding values increase.[4] Consequently, the frontier molecular orbitals of the monomers may be expressed as shown in Figure 4. In this case, the level of the SOMO of the polymer radical might be regarded as constant regardless of the substituents. Because the substituents that lower the difference in eigenvalue between the SOMO and HOMO ought to increase the reactivity of the radical and the monomer, it is obvious that the reaction parameter ρ is negative. In other words, in terms of eq 1, since $E_p^{\ddagger}$ is lower, the eigenvalue of the LUMO of the monomer is further from that of the SOMO of the polymer radical, ρ is negative.

**Table IV**
**Polymerization of 5–9**

| monomer no. | X | init (3 mol %) | solv (5 equiv) | temp, °C | time, h | polym[a] composition I/II | yield,[b] % | IR (C=O), $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 5 | $OCH_3$ | AIBN | | 60 | 20 | 11/89 | 67 | 1693, 1705 |
| | | AIBN | PhH | 60 | 72 | 6/94 | 75 | 1693 |
| | | DTBP | | 120 | 12 | 4/96 | 90 | 1693, 1705 |
| | | DTBP | PhCl | 120 | 24 | 3/97 | 92 | 1697, 1705 |
| 6 | $CH_3$ | AIBN | | 60 | 20 | 9/91 | 46 | 1693, 1705 |
| | | AIBN | PhH | 60 | 72 | 7/93 | 63 | 1693, 1705 |
| | | DTBP | | 120 | 12 | 2/98 | 89[c] | 1693, 1705 |
| | | DTBP | PhCl | 120 | 24 | 1/99 | 90 | 1693, 1705 |
| 7 | H | AIBN | | 60 | 20 | 18/82 | 8 | 1709 |
| | | AIBN | PhH | 60 | 72 | 7/93 | 36[d] | 1697, 1705 |
| | | DTBP | | 120 | 12 | 3/97 | 91[e] | 1693, 1705 |
| | | DTBP | PhCl | 120 | 24 | 0/100 | 90 | 1693 |
| 8 | Cl | AIBN | | 60 | 20 | 15/85 | 3 | 1693, 1707 |
| | | AIBN | PhH | 60 | 72 | 9/91 | 19 | 1693, 1707 |
| | | DTBP | | 120 | 12 | 4/96 | 52[f] | 1693, 1705 |
| | | DTBP | PhCl | 120 | 24 | 4/96 | 49 | 1693, 1705 |
| 9 | CN | AIBN | PhH | 60 | 72 | monomer recovered | | |
| | | DTBP | PhCl | 120 | 24 | 4/96 | 53 | 1697, 1705 |

[a] Estimated by $^1H$ NMR. [b] Insoluble part in ether or a mixture of ether and triethylamine (9/1). [c] $[\eta] = 1.70$ dL/g. [d] $[\eta] < 0.1$ dL/g. [e] $[\eta] = 1.28$ dL/g. [f] $[\eta] = 0.36$ dL/g.

**Scheme II**




In the radical ring-opening polymerization of **5–9**, the substituent effect on $E_p^*$ can be estimated by the electronic property of the substituent in terms of eq 1 without molecular orbital calculation of monomers and radicals, because the polymer radical which attacks the monomers is only one regardless of the monomers.

## Experimental Section

$^1H$ NMR spectra were recorded on a JEOL JNM-PMX 60 SI (60 MHz) or on a JEOL JNM-FX 100 (100 MHz). $^{13}C$ NMR spectra were recorded on a JEOL JNM-FX 100 (25.00 MHz) at a concentration of $2.098 \times 10^{-3}$ mol $mL^{-1}$ at 25 °C. IR spectra were recorded on a Jasco FT/IR 3. Wako silica gel (Wako C-200 or C-300) was used for a column chromatography. $R_f$ values of all compounds on TLC were used for reference only. Melting point was measured on a hot-stage microscope and was not corrected.

## Syntheses of Monomers

**2,2-(4,4′-Dimethoxydiphenyl)-4-(chloromethyl)-1,3-dioxolane (1).** A solution of **12** (6.39 g, 0.058 mol) and 4,4′-dimethoxybenzophenone[5] (14.00 g, 0.058 mol) in xylene (74 mL) was refluxed for 9 h in the presence of *p*-toluenesulfonic acid (*p*-TsOH) (0.10 g) with azeotropic removal of water. Then, *p*-TsOH was quenched by addition of triethylamine (0.15 mL), and xylene was removed under reduced pressure. The residue was purified by column chromatography on silica gel (C-300, benzene, $R_f$ 0.71) to give 18.34 g of **1** as a viscous oil: yield 73%; IR (neat) 3067, 1572, 1200, 1170, 1060, 829 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) δ 7.42–7.08, 6.87–6.53 (m, 8 H, Ar H's), 4.53–3.12 (m, 11 H, $ClCH_2CHCH_2$, $CH_3O$).

**2,2-(4,4′-Dimethyldiphenyl)-4-(chloromethyl)-1,3-dioxolane (2).** **2** was prepared from 4,4′-dimethylbenzophenone[6] and **12** according to the above procedure and purified by column chromatography on silica gel (C-200, benzene, $R_f$ 0.80): yield 62% (viscous oil); IR (neat) 3021, 2904, 2873, 1507, 1072, 1018, 811 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) δ 7.42, 7.29, 7.13, 7.00 (dd, 8 H, Ar H's), 4.60–3.35 (m, 5 H, $ClCH_2CHCH_2$), 2.32 (s, 6 H, $CH_3$).

**2,2-Diphenyl-4-(chloromethyl)-1,3-dioxolane (3).** **3** was prepared according to the procedure described previously.[7]

**2,2-(4,4′-Dichlorodiphenyl)-4-(chloromethyl)-1,3-dioxolane (4).** **4** was prepared from 4,4′-dichlorobenzophenone and **12** according to the procedure of preparation of **2** and purified by column chromatography on silica gel (C-200, carbon tetrachloride, $R_f$ 0.73): yield 54% (oil); IR (neat) 2934, 2867, 1480, 1088, 1010, 820 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) δ 7.80–6.85 (m, 8 H, Ar H's), 4.70–3.12 (m, 5 H, $ClCH_2CHCH_2$).

**2,2-(4,4′-Dimethoxydiphenyl)-4-methylene-1,3-dioxolane (5).** A solution of **1** (31.80 g, 0.10 mol) and potassium *tert*-butoxide (22.40 g, 0.20 mol) in *N*,*N*-dimethylformamide (DMF) (139 mL) was stirred for 6 h at room temperature and poured into water, followed by extraction with five portions of ether. The organic layer was

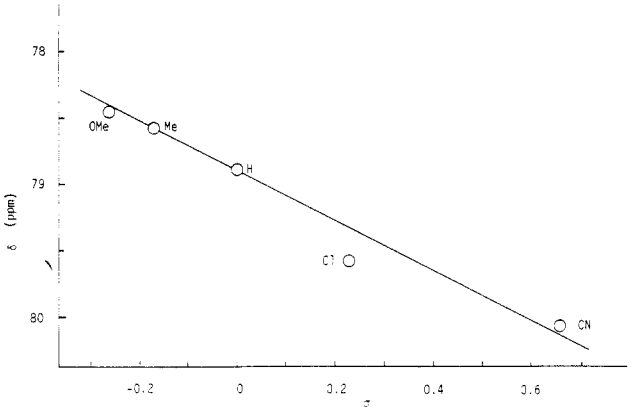



**Figure 2.** Chemical shift of $CH_2$=C in $^{13}C$ NMR spectra of **5**–**9** as a function of Hammett $\sigma$ values.

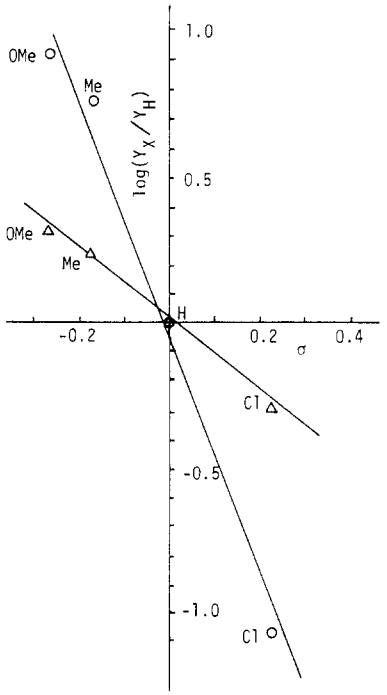



**Figure 3.** Hammett plot of yields in polymerization at 60 °C. ○: in bulk, $\rho$ = −4.2. △: in benzene, $\rho$ = −1.4. $Y_x$: polymer yield from **5**, **6**, **8**, and **9**. $Y_H$: polymer yield from **7**.

washed by water three times and dried over magnesium sulfate, and ether was removed by evaporation. The residue was purified by column chromatography (C-200, benzene/isopropylamine = 9/1, $R_f$ 0.67) to give 28.00 g of **5** as a viscous oil: yield 93%; IR (neat) 2959, 2935, 2835, 1686, 1072, 1033, 833 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 7.47, 7.32, 6.91, 6.75 (dd, 8 H, Ar H's), 4.52–4.38 (m, 3 H, $OCH_2$, C=CH), 4.00–3.69 (m, 7 H, C=CH, $OCH_3$); $^{13}C$ NMR ($CDCl_3$, 25.00 MHz) $\delta$ 159.81, 56.06, 132.72, 127.99, 113.41, 119.90, 78.47, 66.67, 55.12. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.70; H, 6.03.

**2,2-(4,4′-Dimethyldiphenyl)-4-methylene-1,3-dioxolane (6).** **6** was prepared from **2** according to the above procedure and purified by column chromatography on silica gel (C-300, *n*-hexane/triethylamine = 9.5/0.5, $R_f$ 0.84): yield 96% (viscous oil); IR (neat) 3028, 2920, 2868, 1686, 1072, 1022, 814 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 7.38, 7.25, 7.13, 7.00 (dd, 8 H, Ar H's), 4.55–4.32 (m, 3 H, $OCH_2$, C=CH), 3.97–3.77 (m, 1 H, C=CH), 2.30 (s, 6 H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 25.00 MHz) $\delta$ 155.96, 138.32, 137.68, 128.81, 126.33, 111.95, 78.57, 66.72, 21.10. Anal. Calcd for $C_{18}H_{18}O_2$: 81.17; H, 6.81. Found: C, 80.97; H, 6.79.

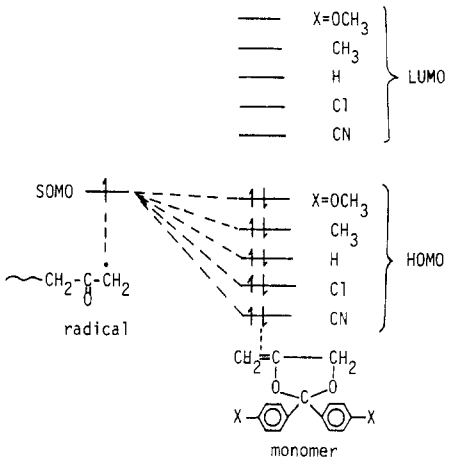



**Figure 4.** Frontier molecular orbitals of the radical and the monomers.

**2,2-Diphenyl-4-methylene-1,3-dioxolane (7).** **7** was prepared according to the procedure described previously:[7] $^{13}C$ NMR ($CDCl_3$, 25.00 MHz) $\delta$ 155.77, 140.46, 128.57, 128.13, 126.33, 111.71, 78.86, 66.72.

**2,2-(4,4′-Dichlorodiphenyl)-4-methylene-1,3-dioxolane (8).** A solution of **4** (18.47 g, 0.054 mol) and sodium methoxide (5.83 g, 0.108 mol) in DMF (72 mL) was stirred for 3 h at 50 °C and poured into water, followed by extraction with five portions of ether. The organic layer was washed by water twice and dried over magnesium sulfate, and ether was removed by evaporation. The residue was distilled under reduced pressure to give 10.79 g of **8**: yield 65%; bp 120–121 °C (0.05 mmHg); IR (neat) 3090, 2959, 2874, 1689, 1091, 1072, 1014, 821 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 7.47–7.10 (m, 8 H, Ar H's), 4.58–4.43 (m, 3 H, $OCH_2$, C=CH), 4.03–3.85 (m, 1 H, C=CH); $^{13}C$ NMR ($CDCl_3$, 25.00 MHz) $\delta$ 155.18, 138.66, 131.25, 128.47, 127.74, 110.68, 79.59, 66.67. Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94; Cl, 23.08. Found: C, 62.91; H, 3.97; Cl, 23.52.

**2,2-(4,4′-Dicyanodiphenyl)-4-methylene-1,3-dioxolane (9).** A solution of **12** (11.40 g, 0.100 mol) and 4,4′-dicyanobenzophenone (**10**)[8] (24.00 g, 0.100 mol) in xylene (140 mL) was refluxed for 9 h in the presence of *p*-TsOH (1.96 g) with azeotropic removal of water. After *p*-TsOH was quenched by addition of triethylamine (3 mL), the solution was cooled to room temperature, and recovered **10** was precipitated and filtered off. After xylene in the filtrate was removed in reduced pressure, a solution of the residue, which was a mixture of 2,2-(4,4′-dicyanodiphenyl)-4-(chloromethyl)-1,3-dioxolane (**11**) and **10** (80/20), and potassium *tert*-butoxide (11.60 g) in DMF (60 mL) was stirred for 6 h at room temperature and poured into water followed by extraction with five portions of ether. The organic layer was washed by water twice and dried over magnesium sulfate, and ether was removed by evaporation. The residue was purified by column chromatography on silica gel (C-300, carbon tetrachloride/methylene chloride/ethyl acetate = 8/1/1, $R_f$ 0.76) to give 12.96 g of **9**: overall yield 45%; mp 127–128 °C; IR (KBr) 2982, 2930, 2878, 2229, 1693, 1072, 829 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) $\delta$ 7.60 (s, 8 H, Ar H's), 4.60–4.42 (m, 3 H, $OCH_2$, C=CH), 4.08–3.92 (m, 1 H, C=CH); $^{13}C$ NMR ($CDCl_3$, 25.00 MHz) $\delta$ 154.30, 144.41, 132.32, 126.72, 118.14, 112.88, 109.66, 80.71, 66.72. Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 75.18; H, 4.12; N, 9.86.

### Polymerization of 5-9

Polymerizations were carried out in sealed tubes at 60 °C in bulk or benzene using AIBN (3 mol %) and at 120 °C in bulk or in chlorobenzene using di-*tert*-butyl peroxide (DTBP) (3 mol %) as an initiator. The polymers obtained at 60 °C in bulk and benzene were purified by dissolution in hot DMSO (80 °C; the polymers from **5**, **6**, **8**) or *m*-cresol (the polymers from **7**), followed by precipitation in ether (the polymers from **5**, **6**, **8**) or a mixture of ether and triethylamine (9/1) (the polymers from **7**). The polymers obtained at 120 °C were purified by dissolution in hot DMSO (130 °C, the polymers from **5**, **6** in bulk and chlorobenzene, **8** in bulk; 120 °C, the polymers from **9**) or in *m*-cresol (the polymers from **7** in bulk and chlorobenzene, **8** in chlorobenzene), followed by precipitation in ether (the polymers from **5**, **6** in bulk and chlorobenzene, **8** in bulk, **9**) or a mixture of ether and triethylamine (9/1) (the polymers from **7** in bulk and chlorobenzene, **8** in chlorobenzene). The precipitated polymers were separated by filtration, thoroughly washed with ether, and dried under reduced pressure at room temperature.

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**Registry No.** 1, 123640-21-1; **2**, 86184-69-2; **3**, 22195-38-6; **4**, 86184-54-5; **5**, 123640-22-2; **5** (homopolymer), 123640-33-5; **6**, 123640-23-3; **6** (homopolymer), 123640-34-6; **7**, 108121-82-0; **7** (homopolymer), 108121-83-1; **8**, 123640-24-4; **8** (homopolymer), 123640-35-7; **9**, 123640-25-5; **9** (homopolymer), 123640-36-8; **12**, 96-24-2; AIBN, 78-67-1; benzoyl peroxide, 94-36-0; 4,4′-dimethoxybenzophenone, 90-96-0; 4,4′-dimethylbenzophenone, 611-97-2; 4,4′-dichlorobenzophenone, 90-98-2.

### References and Notes

(1) Hiraguri, Y.; Endo, T. *J. Am. Chem. Soc.* **1987**, *109*, 3779.
(2) (a) Walling, C.; Briggs, E. R.; Wolfstrin, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537. (b) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Makromol. Chem.* **1965**, *86*, 217. (c) Kinoshita, M.; Imoto, M. *Kogyo Kagaku* Zasshi **1965**, *68*, 2454. (d) Imoto, M.; Takemoto, K. *Nippon Kagaku Kaishi* **1975**, 177; *Chem. Abstr.* **1975**, *82*, 98529u. (e) Giese, B.; Meister, J. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 178.
(3) (a) Imoto, M.; Ouchi, T. *Nippon Kagaku Kaishi* **1986**, 585; *Chem. Abstr.* **1986**, *104*, 225278n. (b) Imoto, M.; Ouchi, T. *Nippon Kagaku Kaishi* **1987**, 894; *Chem. Abstr.* **1987**, *107*, 23785b.
(4) (a) Henri, R. O.; Texier, F. *J. Chem. Educ.* **1978**, *55*, 437. (b) Imoto, M.; Nagaya, T. In *Yuukihannouron*; Tokyo Kagaku Dojin: Tokyo, 1982; p 411.
(5) Klemm, L. H.; Bower, G. W. *J. Org. Chem.* **1957**, *23*, 344.
(6) Noguchi, A.; Igawa, T.; Shimada, Y. *Yuki Gosei Kagaku Kyokaishi* **1963**, *21*, 377; *Chem. Abstr.* **1963**, *59*, 5060f.
(7) Hiraguri, Y.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* in press.
(8) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1977**, *55*, 2286.

# Liquid Crystalline Polyethers Based on Conformational Isomerism. 6.† Influence of Copolymer Composition of a Ternary Copolyether Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane, 1,5-Dibromopentane, 1,7-Dibromoheptane, and 1,9-Dibromononane on Its Mesomorphic Phase Transitions

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ABSTRACT: Ternary copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE), 1,5-dibromopentane, 1,7-dibromoheptane, and 1,9-dibromononane [MBPE-5/7/9($A/B/C$)] were synthesized, and their mesomorphic phase behavior was characterized by differential scanning calorimetry and optical polarized microscopy. Three-dimensional representations of experimental data demonstrated that isomorphic–mesomorphic phase transition temperatures and enthalpy changes of all copolymers are situated on planar surfaces that represent the weight-averaged values of the corresponding thermal transitions and enthalpy changes of the MBPE-5, MBPE-7, and MBPE-9 homopolymers.

### Introduction

Progress in the field of liquid crystalline polymers requires substantial improvements of our ability to tailor-make well-defined main-chain and side-chain liquid crystalline polymers. The relationship structure-phase transitions–properties in main-chain liquid crystalline polymers is one of the multiple problems that continue to demand additional and systematic investigation.

The most reliable and simple synthetic technique that is used to manipulate the structure of polymers, and the least understood in the field of liquid crystalline polymers is copolymerization.[1-4] Main-chain liquid crystalline polymers and copolymers are synthesized by step polymerizations that are based on reversible or irreversible reactions. In contrast to chain copolymerizations, step copolymerizations performed in a homogenous phase

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