

Synthesis, Methanolysis, and Asymmetric Polymerization of *meta*- and *para*-substituted Triphenylmethyl Methacrylates

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(Received March 12, 1987)

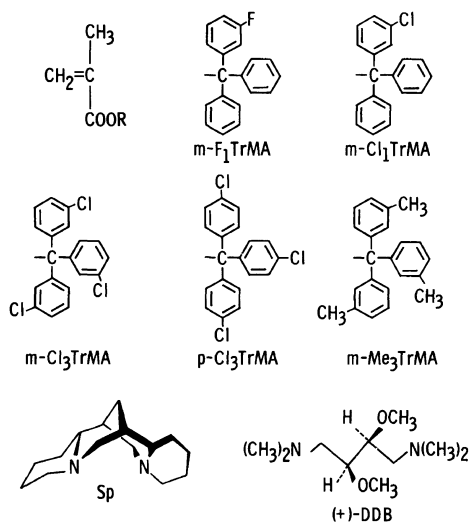
ABSTRACT: Five novel *meta*- and *para*-substituted triphenylmethyl methacrylates, diphenyl-*m*-fluorophenylmethyl methacrylate (*m*-F₁TrMA), *m*-chlorophenyldiphenylmethyl methacrylate (*m*-Cl₁TrMA), tris(*m*-chlorophenyl)methyl methacrylate (*m*-Cl₃TrMA), tris(*p*-chlorophenyl)methyl methacrylate (*p*-Cl₃TrMA), and tris(*m*-tolyl)methyl methacrylate (*m*-Me₃TrMA), were synthesized: Their solvolysis rates were measured in CDCl₃-CD₃OD (1 : 1) by ¹H NMR spectroscopy at 35°C. The rates were greatly affected by the substituents. Chlorine and fluorine substituents decreased the rates of the methanolysis and the methyl group accelerated it. These methacrylates were polymerized with chiral anionic initiators, such as (+)-(2*S*,3*S*)- or (-)-(2*R*,3*R*)-dimethoxy-1,4-bis(dimethylamino)butane (DDB)-*N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) and (-)-sparteine-fluorenyllithium (Sp-FiLi) complexes in toluene at -78°C. DDB-DPEDA-Li complex was more reactive than the Sp-FiLi complex and gave quantitatively optically active, isotactic polymers with one-handed helicity except for *p*-Cl₃TrMA. *p*-Cl₃TrMA did not form a high polymer probably because of the bulkiness of the ester group. The CD spectra of the optically active polymers were different from each other. The copolymerization of *p*-Cl₃TrMA with TrMA by (+)-DDB-DPEDA-Li complex gave a low-molecular-weight copolymer of low optical activity which decreased slowly with time probably because of uncoiling of the helix.

KEY WORDS Asymmetric Polymerization / Anionic Polymerization / Triphenylmethyl Methacrylate / Triphenylmethyl Methacrylate Derivatives / Solvolysis / (-)-Sparteine / 2,3-Dimethoxy-1,4-bis(dimethylamino)butane / Optically Active Polymer / Helix / Optical Resolution /

Optically active poly(triphenylmethyl methacrylate) [poly(TrMA)] is the first example of optically active vinyl polymer with chirality arising only from the one-handed helical structure of a polymer chain and can be directly prepared by asymmetric polymerization of TrMA with chiral anionic initiators such as (-)-sparteine (Sp)-*n*-butyllithium (*n*-BuLi),^{1,2} Sp-fluorenyllithium (Sp-FiLi),^{3,4} and (+)-(2*S*,3*S*)- or (-)-(2*R*,3*R*)-dimethoxy-1,4-bis(dimethylamino)butane (DDB)-lithium amide complexes.⁵ The latter two initiators gave poly(TrMA) having almost pure one-handed helicity. The optically active poly(TrMA) is useful for resolving various

racemic compounds^{6,7} as a chiral stationary phase for high-performance liquid chromatography (HPLC), particularly when it is adsorbed on macroporous silica gel.^{8,9} The chiral stationary phase can resolve many racemic compounds including hydrocarbons, esters, amides, alcohols, and so on, most of which are difficult to be resolved by other methods.¹⁰ As eluents, polar solvents like methanol are more effective rather than nonpolar ones like hexane, indicating that the nonpolar interaction between the polymer, probably triphenylmethyl groups, and nonpolar group of enantiomers plays an important role for effective chiral recognition.¹⁰ However, when methanol

is used as an eluent, the ester groups of poly(TrMA) are slowly solvolyzed to form methyl triphenylmethyl ether.⁹ In order to lessen this defect and also to study the influence of substituents on optical resolving power, we prepared five novel *meta*- or *para*-substituted triphenylmethyl methacrylates, diphenyl-*m*-fluorophenylmethyl methacrylate (*m*-F₁TrMA), *m*-chlorophenyldiphenylmethyl methacrylate (*m*-Cl₁TrMA), tris(*m*-chlorophenyl)methyl methacrylate (*m*-Cl₃TrMA), tris(*p*-chlorophenyl)methyl methacrylate (*p*-Cl₃TrMA), and tris(*m*-tolyl)methyl methacrylate (*m*-Me₃TrMA). In this article, we describe the syntheses, methanolyses, and asymmetric polymerization of these triphenylmethyl methacrylate derivatives.



EXPERIMENTAL

Materials

Syntheses of TrMA Derivatives. The methacrylates were synthesized from silver methacrylate and the corresponding triphenylmethyl chlorides in diethyl ether in a similar manner to the synthesis of TrMA¹¹ and recrystallized from diethyl ether and hexane. The triphenylmethyl chlorides were prepared by the procedure described by Lichtin *et al.*¹² with slight

modification. As an example, the synthesis of *m*-Cl₃TrMA is described. Tris(*m*-chlorophenyl)methanol was prepared by adding methyl *m*-chlorobenzoate to *m*-chlorophenylmagnesium bromide (2.5 eq) in dry benzene under dry nitrogen. The reaction mixture was stirred on a steambath for several hours, and quenched with cold saturated aqueous ammonium chloride. The benzene solution was decanted and the residue was washed with ether. The combined extracts were dried over magnesium sulfate. After removal of the solvents, the residue was recrystallized from methanol to give tris(*m*-chlorophenyl)methanol in about 90% yield. The carbinol was converted to the corresponding chloride with thionyl chloride in dry benzene under dry nitrogen. After the benzene was replaced with diethyl ether, the chloride was allowed to react with silver methacrylate under dark condition. After workup, *m*-Cl₃TrMA was purified by recrystallization from diethyl ether and hexane; yield 65%. The characteristics of triphenylmethyl methacrylate derivatives are listed in Table I. Elemental analyses of the methacrylates were in good agreement with their calculated values within error of 0.3% for carbon, 0.08% for hydrogen, and 0.15% for chlorine.

Fluorenyllithium (FlLi) and *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) were synthesized from fluorene and *N,N'*-diphenylethylenediamine, respectively, with an equivalent amount of *n*-BuLi in toluene. The former salt was soluble in toluene and the latter was scarcely soluble in toluene but became soluble in the presence of a chiral ligand.

(-)-Sparteine (Sigma), (+)- and (-)-DDB (Aldrich) were stirred with calcium hydride overnight and distilled under reduced pressure. Toluene was purified in the usual manner, and distilled under vacuum in the presence of *n*-BuLi just before use.

Table I. Characteristics of triphenylmethyl methacrylate derivatives

Monomer	mp °C	IR (Nujol)/ cm ⁻¹		¹ H NMR/ppm ^a			¹³ C NMR/ppm ^b				
		C=O	C=C	α-CH ₃	CH ₂ =		α-CH ₃	CH ₂ =	=C	C=O	⊠-C-
TrMA	103.0–103.5	1726	1634	1.96	5.57	6.20	18.55	125.52	137.41	165.12	89.91
<i>m</i> -F ₁ TrMA	85.2– 85.6	1720	1636	1.96	5.54	6.20	18.52	125.80	137.23	165.02	89.37
<i>m</i> -Cl ₁ TrMA	78.5– 79.5	1726	1635	1.91	5.60	6.23	18.52	125.80	137.18	165.00	89.30
<i>m</i> -Cl ₃ TrMA	123.4–124.0	1727	1634	1.97	5.63	6.24	18.44	126.36	136.73	164.73	88.01
<i>p</i> -Cl ₃ TrMA	140.5–141.5	1722	1635	1.92	5.58	6.16	18.44	126.05	136.88	164.94	88.39
<i>m</i> -Me ₃ TrMA	141.0–142.0	1728	1636	1.97	5.58	6.22	18.61	125.29	137.58	165.12	90.03

^a In CCl₄, 35°C, TMS.^b In CDCl₃, 27°C, TMS.

Polymerization Procedure

Polymerization was carried out in a dry glass ampule under dry nitrogen. A monomer was placed in an ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, toluene was added with a hypodermic syringe and then cooled to –78°C. An initiator solution, which was prepared by mixing FILi or DPEDA–Li with 1.2 eq of a chiral ligand in toluene at room temperature just before use, was then added to the monomer solution with a syringe. The polymerization was terminated by the addition of a small amount of methanol and the reaction mixture was poured in a large amount of methanol. The polymer was separated by centrifugation and dried as quickly as possible to avoid methanolysis. The polymer was then dissolved in tetrahydrofuran (THF) and added dropwise into a mixture of benzene–hexane (1:1, v/v) to separate oligomers as the soluble part.

Polymerization in a 1.0-cm optical cell was carried out in the same manner and the change of optical rotation in the polymerization system at –78°C was directly followed. In order to determine the tacticity and molecular weight, the polymers were converted to poly(methyl methacrylate) (PMMA) by methylation with diazomethane of the poly(methacrylic acid)

after hydrolyzed with hydrochloric acid in methanol.

Solvolysis in Methanol

The solvolysis rates of methacrylates were measured in an NMR sample tube by means of ¹H NMR spectroscopy in CDCl₃–CD₃OD (1:1, v/v) at 35°C. The relative intensities of olefinic protons of a monomer to hydrolyzed methacrylic acid were used for estimating the solvolysis rates.

Measurements

Optical rotation was measured with a JASCO DIP-181 polarimeter at 25°C. ¹H NMR and ¹³C MNR spectra were obtained on a JNM-MH-100 (100 MHz) and JEOL FX-100 (25 MHz) instruments, respectively. Tetramethylsilane (TMS) was used as the internal standard. Gel permeation chromatographic analysis was accomplished on a JASCO TRI ROTAR-II equipped with UV and polarimetric (JASCO DIP-181C) detectors and a JASCO FLC-A10 equipped with an RI (SHODEX SE-11) detector using THF as the eluent. Two Shodex GPC columns, A80M (50 cm × 2) were connected in series. The molecular weight calibration curves were obtained with polystyrene standards. The molecular weight of poly(triphenylmethyl methacrylate)s was estimated from the GPC curve of the

PMMA derived from them. Circular dichroism (CD) spectra were measured with a JASCO J40-CD apparatus equipped with a computerized data processor.

RESULTS AND DISCUSSION

Solvolysis of Monomer by Methanol

It is well known that triphenylmethyl chloride derivatives react with alcohol to form corresponding ethers and the rates of alcoholysis are affected by the substituents on phenyl groups.¹³ Brown and Okamoto¹⁴ reported that the rates of solvolysis of substituted triphenylmethyl chlorides decrease by introducing electron-withdrawing groups such as halogens, cyano, and nitro groups, and are accelerated by electron-donating groups like methyl group. Meta substitution was more effective than *ortho* or *para* substitution. It has been shown that in the solvolysis of esters of tertiary alcohols, oxygen-carbon bonds are cleaved as in the solvolyses of substituted triphenylmethyl chlorides.¹⁵ These results suggest that meta halogen-substituted triphenylmethyl methacrylates would be more stable against alcoholysis than TrMA, giving optically active polymers with higher durability against methanol than poly(TrMA) as chiral stationary phases for HPLC. We synthesized five *meta*- or *para*-substituted triphenylmethyl methacrylates, and the solvolysis rates were measured in CDCl₃-CD₃OD (1:1, v/v) at 35°C by means of ¹H NMR spectroscopy. The first-order plots are shown in Figure 1. The values of the rate constants (*k*) and half-life periods are shown in Table II. The introduction of *meta* halogen groups greatly decreased the solvolysis rates and the *meta* methyl group increased it.

In Figure 2 is shown a plot of $\log(k/k_H)$ for the solvolysis *versus* Hammett's substituted constant (σ^+) introduced by Brown and Okamoto in the case of the electrophilic substituent reaction like the solvolysis of the

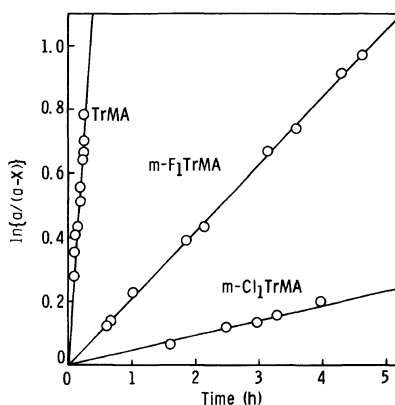


Figure 1. Methanolysis of triphenylmethyl methacrylate derivatives in CDCl₃-CD₃OD (1:1) at 35°C.

Table II. Methanolysis of methacrylates in CDCl₃-CD₃OD (1:1, v/v) at 35°C^a

Methacrylate	<i>k</i> ^b h ⁻¹	Half-life	log <i>k</i> / <i>k</i> _H
		period min	
<i>m</i> -Me ₃ TrMA	13.0	3.2	0.66
TrMA	2.86	14.5	0
<i>m</i> -F ₁ TrMA	0.21	198	-1.13
<i>m</i> -Cl ₁ TrMA	0.045	930	-1.77
<i>m</i> -Cl ₃ TrMA	0.053	786	-1.73
<i>p</i> -Cl ₃ TrMA	0.056	744	-1.71

^a Concentration: 0.39–0.40 mol l⁻¹.

^b Rate constant.

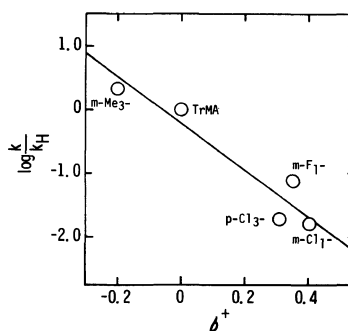


Figure 2. Plots of $\log(k/k_H)$ *versus* Hammett's substituted constant (σ^+) in methanolysis of triphenylmethyl methacrylate derivatives in CDCl₃-CD₃OD (1:1) at 35°C.

Asymmetric Polymerization of TrMA Derivatives

Table III. Asymmetric polymerization of triphenylmethyl methacrylate derivatives in toluene at $-78^{\circ}\text{C}^{\text{a}}$

Monomer	/g	Initiator	Time h	Yield %	$[\alpha]_{\text{D}}^{25\text{b}}$	B/H ^c -insoluble		B/H ^c -soluble		\bar{M}_n^{d} $\times 10^{-3}$	$\frac{\bar{M}_w}{\bar{M}_n^{\text{d}}}$	Tacticity/% ^d		
						Yield %	$[\alpha]_{\text{D}}^{25\text{b}}$	Yield %	$[\alpha]_{\text{D}}^{25\text{b}}$			I	H	S
TrMA	1	(-)-DDB-DPEDA-Li	2	100	-325	88	-354	12	-21	4.5		98	2	0
	1	(-)-Sp-FILi	24	100	+300	87	+384	13	-20	5.9	1.29	98	2	0
<i>m</i> -F ₁ TrMA	3	(+)-DDB-DPEDA-Li	13	100	+297	87	+330	13	+152	4.5	1.21	96	3	1
	1	(-)-Sp-FILi	18	91	+330	80	+340	11	+95					
<i>m</i> -Cl ₁ TrMA	2	(+)-DDB-DPEDA-Li	4	100	+314	83	+356	17	+70	3.6	1.20	97	3	0
	1	(-)-Sp-FILi	4	45	+221									
<i>m</i> -Cl ₃ TrMA	5	(-)-DDB-DPEDA-Li	25	100	-251	88	-284	12	-21	5.3	1.53	97	2	1
	1	(-)-Sp-FILi	24	23	+10									
<i>p</i> -Cl ₃ TrMA	3	(+)-DDB-DPEDA-Li	7 ^e	56	0							53	44	3
	1	(-)-Sp-FILi	61 ^e	0										
<i>m</i> -Me ₃ TrMA	1.5	(-)-DDB-DPEDA-Li	2	83	-234 ^f	68	-281 ^f	15	-22 ^f	2.6		93 ^g	6 ^g	1 ^g
	1.5	(-)-DDB-PEA-Li ^h	2	76	-267 ^f	63	-310 ^f	13	-50 ^f					
	1.5	(-)-Sp-FILi	24	16	+14 ^f									

^a [Monomer]/[Li] = 20, [Toluene]/[Monomer] = 20 (v/w).

^b In THF.

^c Benzene-hexane (1:1).

^d Estimated from PMMA derived from unfractionated poly(TrMA) derivatives.

^e In days.

^f At 546 nm in CHCl₃.

^g Benzene-hexane (1:1)-insoluble part.

^h Lithium amide of (±)-*N*-(1-phenylethyl)aniline.

substituted triphenylmethyl chlorides.¹⁴ Good relationship was observed. The solvolysis rates may be correlated to the stability of triaryl-methyl cations.¹³ Electron-donating substituents seem to accelerate solvolysis by stabilizing the cations.

Asymmetric Polymerization of TrMA Derivatives

Table III shows the results of the asym-

metric polymerization of six monomers including TrMA using Sp-FILi and (+)- or (-)-DDB-DPEDA-Li complexes as chiral initiators in toluene at -78°C . These chiral initiators gave poly(TrMA) of almost 100% one-handed helicity in the asymmetric polymerization of TrMA.³⁻⁵ The DDB-DPEDA-Li complex was more reactive than the Sp-FILi complex and gave quantitatively optically active polymers of high specific rotation in about

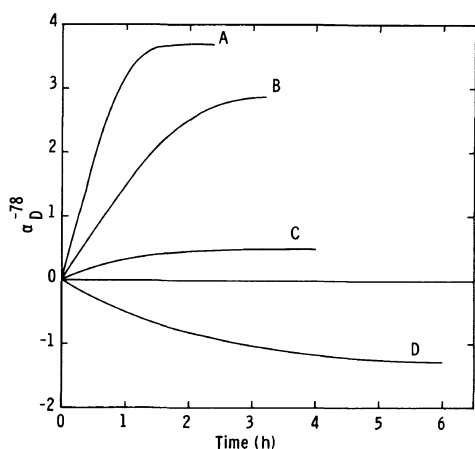


Figure 3. Polymerization of triphenylmethyl methacrylate derivatives with (+)-DDB-DPEDA-Li (A, B, C) and (-)-DDB-DPEDA-Li (D) complexes in a 1.0-cm cell in toluene at -78°C . Toluene, 3 ml; monomer, 0.15 g; [Monomer]/[Li]=20. Total volume of the reaction mixture was about 2.8 ml at -78°C : A, TrMA; B, *m*-Cl₁TrMA; C, *m*-Cl₃TrMA; D, *m*-Me₃TrMA.

24 h except for *p*-Cl₃TrMA. *p*-Cl₃TrMA could not be polymerized to a high-molecular-weight polymer even in a prolonged reaction. Such low reactivity of *p*-Cl₃TrMA seems attributable to the steric effect of the *para*-chlorine atoms because there exist no clear differences in ¹H and ¹³C NMR spectra between *p*-Cl₃TrMA and *m*-Cl₃TrMA as shown in Table I. The specific rotation of the polymers slightly decreased with an increase in the size and number of substituents. The polymers isolated as methanol-insoluble products always contained 10-20% oligomers of low optical activity, which were separated by fractionation with benzene-hexane (1 : 1, v/v). The polymers were highly isotactic except for poly(*p*-Cl₃TrMA) which was a mixture of low-molecular-weight oligomers. Elemental analyses of halogen-substituted poly(triphenylmethyl methacrylate)s showed that almost no side reaction such as halogen abstracting reaction by lithium complexes took place in the polymerization reaction.

Figure 3 illustrates the change of optical rotation of the polymerization systems that was directly monitored in a 1.0 cm optical cell

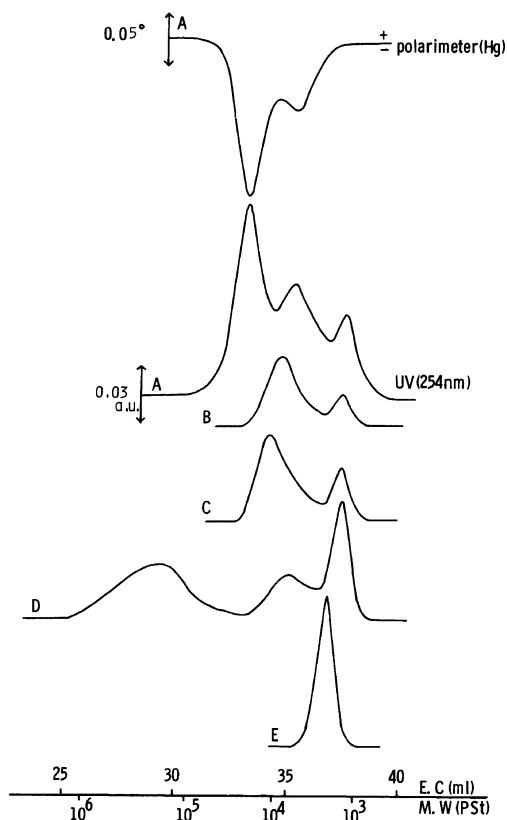


Figure 4. GPC curves of poly(TrMA) derivatives: A, TrMA; B, *m*-F₁TrMA; C, *m*-Cl₁TrMA; D, *m*-Cl₃TrMA; E, *p*-Cl₃TrMA.

using DDB-DPEDA-Li complex in toluene at -78°C . All the systems gave the polymer quantitatively after optical rotation reached a constant value. The final observed rotations of polymers decreased with an increase in number of substituents. The final observed rotation of poly(*m*-Cl₁TrMA) system in toluene at -78°C was about 40% smaller than that of poly(TrMA) system although the specific rotation of the both polymers isolated was almost equal. Furthermore, the final optical rotation of poly(*m*-Cl₃TrMA) system was only about $+0.46^{\circ}$ which was about 1/8 and 1/5 of the values of poly(TrMA) and poly(*m*-Cl₃TrMA) systems, respectively, and the specific rotation of the living polymer at -78°C was calculated to be $+101^{\circ}$ which was sig-

nificantly lower than the value ($[\alpha]_D^{25} + 250^\circ$) after isolation (Table III). This indicates that the specific rotation of poly(*m*-Cl₃TrMA) increased greatly after isolation. The conformation of the polymer formed in the process of polymerization at -78°C may change at higher temperature. Although *m*-Me₃TrMA is sterically similar to *m*-Cl₃TrMA, the final optical rotation of the poly(*m*-Me₃TrMA) at -78°C was much greater than that of poly(*m*-Cl₃TrMA). Poly(*m*-Me₃TrMA) and poly(*m*-Cl₃TrMA) may possess different conformations.

Figure 4 shows the GPC curves of the polymers obtained with the DDB-DPEDA-Li complex in toluene at -78°C (unfractionated polymers in Table III). We previously reported that the GPC curve of poly(TrMA) prepared with Sp-*n*-BuLi complex in toluene at -78°C showed a complicated distribution containing a low-molecular-weight component of low optical activity.² The GPC curve of poly(TrMA) obtained with (-)-DDB-DPEDA-Li also demonstrated a similar complicated distribution pattern (Figure 4(A)). Although two higher-molecular-weight components showed high optical activity, the oligomer of molecular weight less than 2000 was almost optically inactive. The oligomer could be excluded as a soluble part by fractionation with benzene-hexane (1:1, v/v). Other polymers except poly(*p*-Cl₃TrMA) also contained oligomers of low optical activity and showed complicated GPC curves. Poly(*p*-Cl₃TrMA) exhibited almost no optical activity and a simple GPC peak with a narrow distribution at low-molecular-weight region. *p*-Cl₃TrMA might be difficult to polymerize beyond a certain degree of polymerization due to the steric reason.

The CD spectra of the optically active polymers (benzene-hexane-insoluble part in Table III) were measured (Figure 5). The bands at 250–280 nm assigned to the absorption of phenyl groups showed different spectral patterns. The absorption around 240 nm,

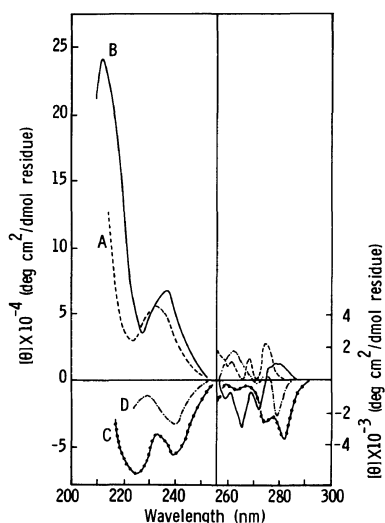


Figure 5. CD spectra of poly(*m*-F₁TrMA) (A), poly(*m*-Cl₁TrMA) (B), poly(*m*-Cl₃TrMA) (C), and poly(*m*-Me₃TrMA) (D) in THF. The benzene-hexane (1:1)-insoluble parts in Table III were used as samples.

which may be due to carbonyl groups, shifted to higher wavelength as the size and number of substituents increased. Previously, we proposed that triphenylmethyl groups in optically active poly(TrMA) likely take either a right- or left-handed propeller structure accompanying the formation of the one-handed helical structure of a polymer chain and such a chiral propeller structure may play an important role for chiral recognition in optical resolution.¹⁶ The differences in CD spectra of these polymers may be attributed to the different propeller structures or conformation of ester groups including carbonyl groups. These differences led to different chiral recognition ability of the polymers in the optical resolution of racemic compounds when used as chiral stationary phase for HPLC, and the results will be reported separately.

Asymmetric Copolymerization

Table IV shows the results of the asymmetric copolymerization of TrMA (M₁) with *m*-Cl₃-, *p*-Cl₃-, and *m*-Me₃TrMA (M₂) by (+)-DDB-DPEDA-Li complex in toluene at

Table IV. Asymmetric copolymerization of TrMA (M_1) with M_2 by (+)-DDB-DPEDA-Li complex in toluene at -78°C^a

M_2	M_1	Time	Yield	$[\alpha]_D^{25b}$
	M_2	h	%	
<i>m</i> -Cl ₃ TrMA	2	22	100	+276
	1	22	100	+275
	0.5	22	100	+255
<i>p</i> -Cl ₃ TrMA	1	4	52	+11
	1	25 ^c	90	+70 ^d (+22) ^e
	1 ^f	73	93	+187 ^d (+151) ^e
<i>m</i> -Me ₃ TrMA ^g	1	24	100	-263 ^h

^a $[M_1 + M_2]/[Li] = 20$.^b In THF.^c In days.^d At 365 nm, $[\alpha]_{365}^{25}/[\alpha]_D^{25} \approx 4$.^e Specific rotation after 4 h is shown in parenthesis.^f At -40°C .^g (-)-DDB was used.^h Rotation ($[\alpha]_D^{25}$) of benzene-hexane (1:1)-insoluble (87%) and -soluble parts (13%) was -289° and -97° , respectively.

-78°C . The specific rotation of poly(TrMA-*co*-*m*-Cl₃TrMA)s was almost the same as that of poly(*m*-Cl₃TrMA), regardless of the molar ratio (M_1/M_2) within the experimental conditions, and the CD spectra of all the copolymers were very similar to that of poly(*m*-Cl₃TrMA). A similar result was also obtained in the copolymerization of *m*-Me₃TrMA with TrMA. Although *p*-Cl₃TrMA could not be polymerized to a high-molecular-weight polymer, copolymerization with TrMA gave the low-molecular-weight copolymer of low optical activity, which decreased slowly with time probably because of uncoiling of the helix.

CONCLUSIONS

Five *meta*- and *para*-substituted triphenylmethyl methacrylates were synthesized. The rates of methanolyses greatly decreased by the introduction of *meta*-halogen groups and in-

creased by methyl group. Therefore, the methacrylates with electron-withdrawing substituents are preferable to obtain more durable chiral stationary phases for HPLC. All methacrylates except for *p*-Cl₃TrMA gave optically active one-handed helical polymers with chiral lithium initiators in toluene at -78°C . *p*-Cl₃TrMA could not be polymerized to a high-molecular-weight polymer. The CD spectra of the optically active polymers were greatly different from each other. The differences of CD spectra may be attributed to the different propeller structures and/or conformations of the ester groups.

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