Polymerization of α,ω-Bis(p-isopropenylphenyl)alkanes by Means of Stannic Chloride

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ABSTRACT: The polymerization of α,ω-bis(p-isopropenylphenyl)alkanes were carried out in rather dilute conditions at -21 to $20°C$, using stannic chloride as a catalyst, and soluble polymers were obtained, although monomers were diolefinic. The cyclopolymerization did not take place, but the addition polymerization did occur, along with the transfer reaction which afforded the indan unit. The direct determination of the content of the indan unit was accomplished by means of IR spectroscopy. The k_{tr}/k_p value was calculated from the observed content by assuming that the transfer was spontaneous. The activation parameters were estimated to be
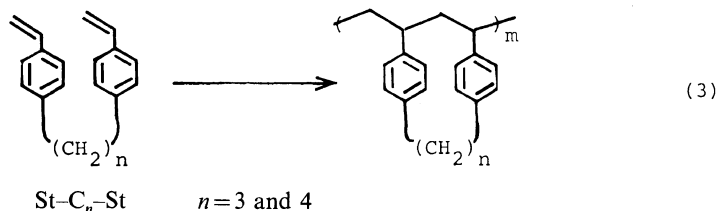A_{tr}/A_p, 6.6×10^5 mol dm^{-3}; $\Delta E_{tr} - \Delta E_p$, 8.8 kcal mol^{-1} (36.8 kJ mol^{-1}).
    KEY WORDS   Cationic Polymerization / Stepwise Polymerization / Bis(p-isopropenylphenyl)methane / α-Methylstyrene / Transfer Reaction / Stannic Chloride /

The stepwise polymerization of α, ω-bis(p-isopropenylphenyl)alkanes and related compounds was discovered first by Mitin *et al.*,[1-3] who treated these compounds with Lewis acids at a relatively high

$$R' = \text{polymer}$$

$$R'' = CH_3\text{- or polymer}$$
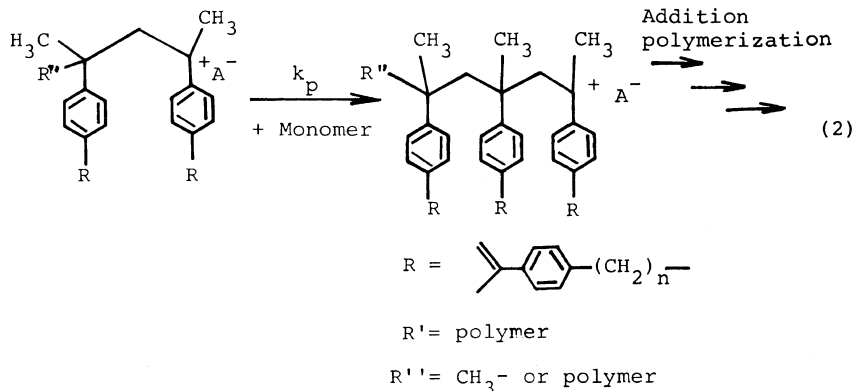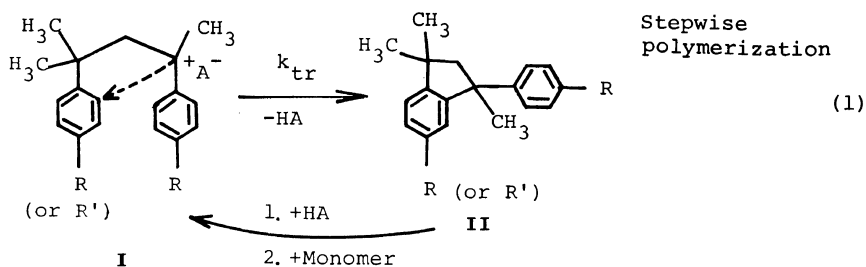
temperature ($> 70°C$). Interesting polymers containing indan units in the main chain[1,3] were formed by the intramolecular electrophilic attack of the cationic site in **I**, as shown in eq 1. Since the polymerization was carried out at a temperature higher than its ceiling temperature, it was difficult for the addition polymerization (2) to occur.

We thought that the compounds might cyclopolymerize at a low temperature, in connection with the cationic cyclopolymerization of α,ω-bis (*p*-vinylphenyl)alkanes (St–C_n–St) to afford a cyclophane-unit-containing polymer, as shown in eq 3.[4,5]

$$(3)$$

St–C_n–St $n = 3$ and 4

However, as will be clear in this paper, α-methylstyrene derivatives (MSt–C_n–MSt, even if $n = 3$) did not cyclopolymerize, and competition between the stepwise polymerization (or transfer) and addition polymerization (or propagation) was observed, as shown in eq 1 and 2.

We succeeded in determining the content of the indan units which resulted from the transfer reaction, so that the evaluation of the competition could be possible. In this paper, we would like to report the structure of the polymer and the relative rate ratio, k_{tr}/k_p, in the polymerization.

EXPERIMENTAL

General

Elemental analyses were done at the Microanalysis Center of Kyoto University. Molecular weight was measured by a Knauer vapor pressure osmometer. NMR spectra were recorded by a Varian Model T-60A NMR spectrometer in deuterochloroform using tetramethylsilane as an internal standard. UV and visible spectroscopies were carried out on a Beckman DB-G grating spectrophotometer. IR spectra were taken by a Hitachi 215 grating IR spectrophotometer. For the determination of double bond content and indan unit content, IR spectra of the polymers were recorded from 1000 to 1750 cm^{-1} using 0.5 mm KBr liquid cells. A typical IR spectrum is shown, with the base lines used for analyses, in Figure 1. Further details are mentioned in the next section.

Materials
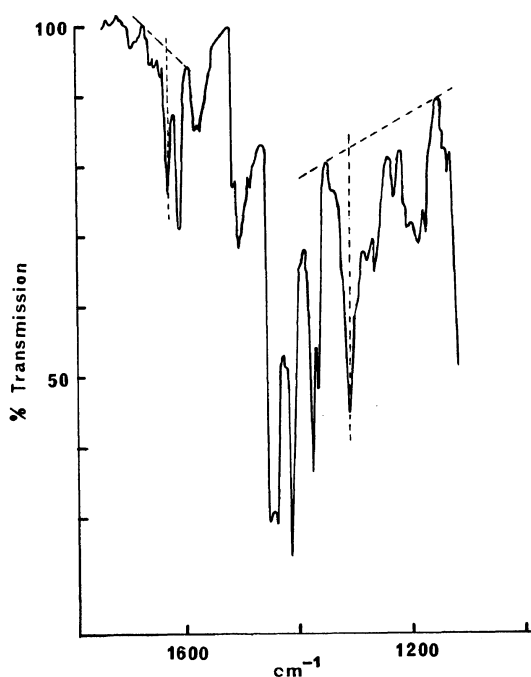
Methylene chloride and 1,2-dichloroethane were

Figure 1. IR spectrum of poly(MSt–C_1–MSt) in benzene solution (0.5 mm KBr-cell).

refluxed over calcium hydride for at least two days and distilled under a nitrogen atmosphere. Other solvents were purified in the usual manner.[6]

Stannic chloride was distilled under a nitrogen atmosphere and used as methylene chloride solution, which was prepared just before use.

Monomers were prepared by the following representative procedure: In 250 ml of ether solution of methylmagnesium iodide made from 3.0 g of magnesium and 8.0 ml of methyl iodide, 150 ml of

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absolute THF solution of 1,2-bis(p-acetylphenyl)ethane (2.5 g) was added dropwise. After the addition, the mixture was heated to reflux for 3 h and then allowed to stand overnight. By the ordinary work-up procedure, 2.61 g of crystalline 1,2-bis[p-(1-hydroxy-1-methylethyl)phenyl]ethane (94%) was obtained; mp 149—151°C (EtOH) (lit.[7] 150°C).

Bis[p-(1-hydroxyl-1-methylethyl)phenyl]methane was obtained quantitatively. 1,3-Bis[p-(1-hydroxy-1-methylethyl)phenyl]propane was obtained in 93% yield; mp 96.0—97.1°C (CH$_3$COOEt).

1,2-Bis[p-(1-hydroxyl-1-methylethyl)phenyl]ethane (1.51 g) and potassium bisulfate (38 mg) were placed in a ballflask, which was heated at 170°C for 30 min in a vacuum produced by an aspirator, and then the product was distilled at 180°C under reduced pressure [0.02 mmHg (3 Pa)]. The yield was 1.15 g (87%). The prepared material, 1,2-bis(p-isopropenylphenyl)ethane, was recrystallized from ethanol; mp 131–132°C (lit.[7] 124.5°C). IR, UV, and NMR data are consistent with the structure.

Bis(p-isopropenylphenyl)methane was obtained in 84% yield; mp 57°C (lit.[7] 57°C). 1,3-Bis(p-isopropenylphenyl)propane was an oily material: bp 164—168°C [0.07 mmHg (9 Pa)]. *Anal.* Calcd for C$_{21}$H$_{24}$: C, 91.25%; H, 8.75%. Found: C, 91.22%; H, 8.87%.

Decadeuterobis(p-isopropenylphenyl)methane (MSt–C$_1$–MSt-d_{10}) was prepared in 79% yield (mp 58—59°C) by the dehydration after methylation of hexadeuterobis(p-acetylphenyl)methane with trideuteromethylmagnesium iodide. Hexadeuterobis(p-acetylphenyl)methane was obtained by means of the base catalyzed hydrogen–deuterium exchange reported by Matsuzaki *et al.*[8] NMR spectroscopic results gave the contents of deuterium as 92% at the

methyl group and 90% at the olefinic methylene group.

Polymerization Procedure

The polymerization was carried out with a vigorous stirring at the prescribed temperature under a nitrogen atmosphere and stopped by the addition of cold ammoniacal methanol. The polymer was precipitated in methanol, collected by filtration, and washed with methanol several times. The dried polymer was brought to a constant weight in a vacuum desiccator.

RESULTS AND DISCUSSION

Structure of the Polymer

Spectral data of poly (MSt–C$_3$–MSt) are summarized in Table I, along with those of poly-(St–C$_3$–St) for comparison. According to NMR and IR spectroscopies, the polymer had indan units (**II**) and residual unsaturation (**I**). However, no evidence was found for the presence of a cyclophane unit in the main chain; *i.e.*, a high field shift of aromatic protons in NMR spectroscopy, an absorption around 240 nm in UV spectroscopy, and the charge-transfer absorption with tetracyanoethylene at 608 nm were not observed. Therefore, it is concluded that cyclopolymerization did not occur in the cationic polymerization of MSt–C$_3$–MSt. The structures of other poly (MSt–C$_n$–MSt) obtained in this work were the same as that of poly(MSt–C$_3$–MSt).

The difference between the polymerizations of two kinds of monomers, MSt–C$_3$–MSt and St–C$_3$–St, is intriguing. The stabilization of the cationic site by a methyl group and/or the steric hindrance against the face-to-face orientation of two α-methylstyrene

Table I. Spectral data of poly (MSt–C$_n$–MSt) and poly(St–C$_3$–St)

	Poly(MSt–C$_n$–MSt)	Poly(St–C$_3$–St)[a]
NMR	Comparison with 1,1,3-trimethyl-3-phenylindan (TMPI)	3.40 τ (aromatic protons)
IR	1306 cm^{-1} (indan, 1315; TMPI, 1306; cyclopentane, 1316)	Comparison with [3.3]paracyclophane[b]
UV	$n=3$; minimum at 240 nm	Absorption at 240 nm; bathochromic shift of B-band and its broadening
Visible	$n=3$; charge-transfer complex with TCNE, λ_{max} 485 nm	Charge-transfer complex with TCNE, λ_{max} 608 nm

[a] Ref 4 and 5.
[b] Provided by Prof. D. J. Cram.

moieties might be the reason(s) which prevent MSt–C_3–MSt from cyclopolymerizing.

Residual Unsaturation in the Polymer

NMR and IR spectroscopies were independently applied for the determination of residual unsaturation in the polymer. Using the NMR spectra, the percentages of the residual unsaturation were calculated from the integrals of methylene protons in the isopropenyl group and the methylene linkage of two aromatic groups in the polymer. One residual isopropenyl group per monomer unit is defined as 100% of residual unsaturation. The determination of the residual unsaturation by IR spectroscopy was carried out by using the absorption at 1625 cm^{-1}, as shown in Figure 1. These two methods were compared and the results agreed fairly well, as shown in Figure 2.

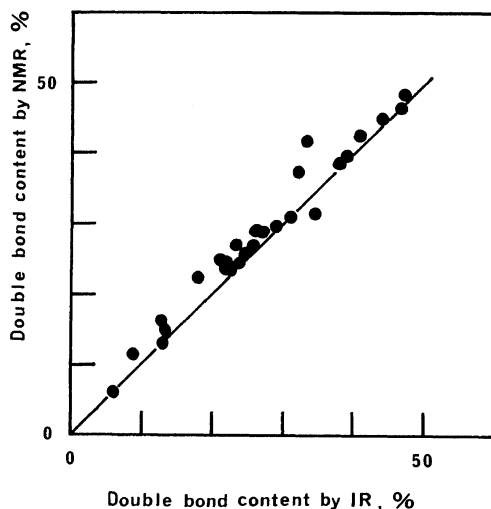In the NMR and IR spectroscopies, no other clear peaks due to the unsaturation in III or IV, which

Figure 2. Relationship between IR and NMR spectroscopic analyses of residual unsaturation in poly-(MSt–C_1–MSt).
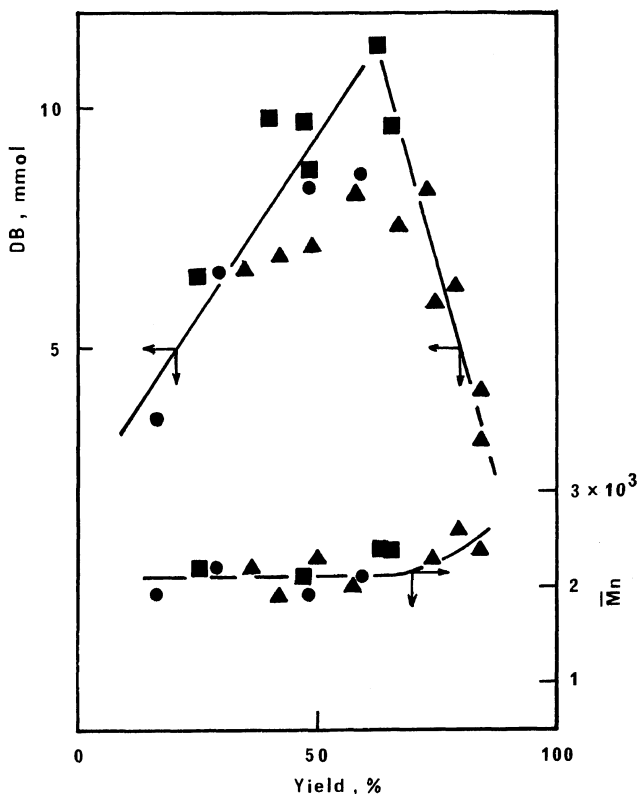

Figure 3. Residual unsaturation (DB) in poly(MSt–C_1–MSt) and $\bar{M}_n$. Polymerization conditions: [M]$_0$, 0.06 mol dm^{-3}; catalyst, SnCl$_4$, 1 mmol dm^{-3}; solvent, CH$_2$Cl$_2$; ■, 0°C; ●, 10°C; ▲, 20°C.
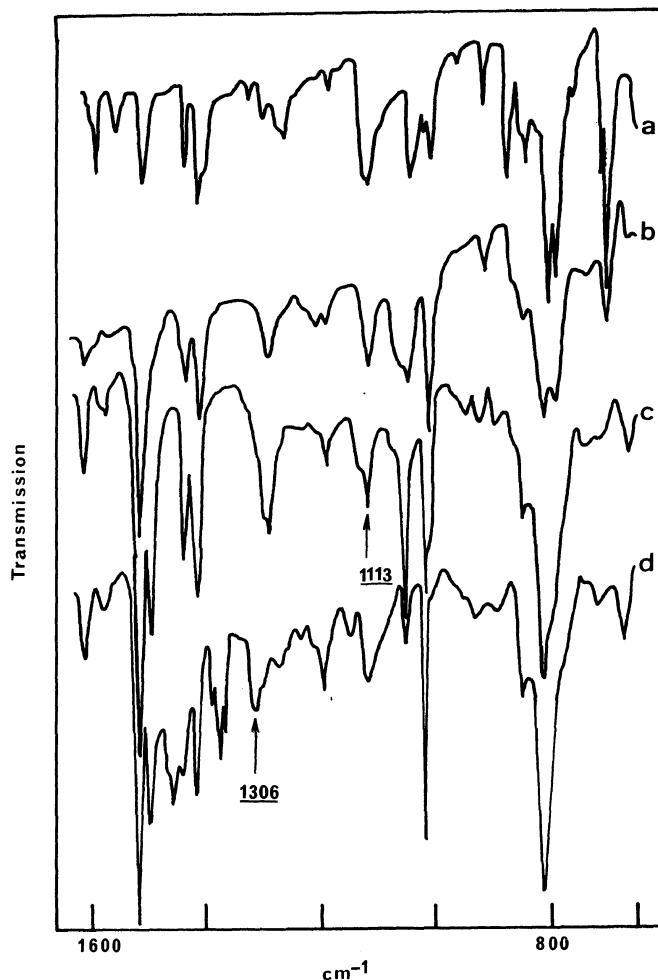
Figure 4. IR spectra (KBr-disk).

a, Decadeuterobis(p-isopropenylphenyl)methane (DDBM).

b, Poly(DDBM). Polymerization conditions: $[M]_0 = 0.06 \text{ mol dm}^{-3}$, $[SnCl_4] = 1 \text{ mmol dm}^{-3}$ in 1,2-dichloro-ethane for 30 s at $-21°C$.

c, Poly(DDBM). Polymerization conditions: $[M]_0 = 0.06 \text{ mol dm}^{-3}$, $[SnCl_4] = 1 \text{ mmol dm}^{-3}$ in 1,2-dichloro-ethane for 15 min at $20°C$.

d, Poly(MSt–C_1–MSt). Polymerization conditions: $[M]_0 = 0.06 \text{ mol dm}^{-3}$, $[SnCl_4] = 1 \text{ mmol dm}^{-3}$ in methylene chloride for 15 min at $20°C$.

would have been made by the spontaneous transfer,[9] were recognized. NMR spectra of polymers show only an isopropenyl group: *i.e.*, two singlets ($=CH_2$) with equal integrals at 4.67 and 4.98 τ and a singlet ($-CH_3$) at 7.88 τ; the integral ratio of the two groups was 1.94 : 3.00.
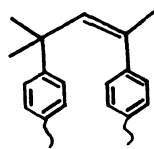
(III)
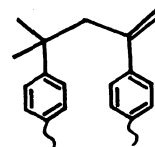
(IV)

In Figure 3, the changes of the residual unsaturation and $\bar{M}_n$ along the polymerization are illustrated. The content of the residual unsaturation increased at first until 65% yield and then decreased sharply, although $\bar{M}_n$ was almost constant until 75% yield. The decrease in the residual unsaturation is considered to be due not to the stepwise polymerization but to the other reactions caused by cationic species. The polymer obtained, however, contained no chlorine (within the experimental error). The decrease in the unsaturation denied the possibility that the per cent content of cyclized parts is equal to the number of 100 minus the per cent content of residual unsaturation.

The Evaluation of k_{tr}/k_p

In order to calculate the transfer constant, k_{tr}/k_p, which can be also considered as the relative rate ratio between the stepwise polymerization and the addition polymerization, the content of indan units in polymers must be determined directly.

The model compound of unit (**II**), 1,1,3-trimethyl-3-phenylindan, showed an IR abosrption at 1306 cm^{-1}. Poly(MSt–C$_1$–MSt) obtained at 20°C in methylene chloride, which seemed to have the highest indan units content among the polymers produced, showed an absorption at 1306 cm^{-1} and no double bond peaks, while poly(MSt–C$_1$–MSt-d_{10}) obtained in the same conditions showed no absorption at 1306 cm^{-1}, but one at 1113 cm^{-1}, as shown in Figure 4. Since the IR absorption of cyclopentane at 1316 cm^{-1} is assigned to the wagging vibration of methylene, and shifts to 1155 cm^{-1} if totally deuterated, the absorption at 1306 cm^{-1} in poly-(MSt–C$_1$–MSt) was considered to be due to indan units.

The absorption due to the isopropenyl group appeared at the same wavenumber as that of the indan unit. Since the absorptions due to olefin and the indan derivative both obeyed Lambert–Beer's law, the two contributions could be separated by the following equation

$$\log (I_0/I) = \varepsilon_d c_d d + \varepsilon_i c_i d \qquad (4)$$
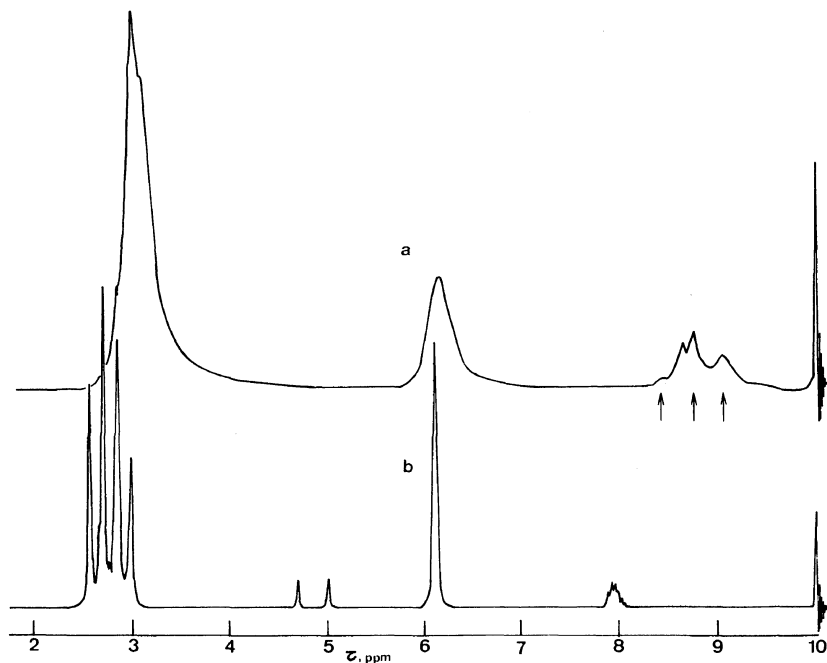

Figure 5. NMR spectra of decadeuterobis(p-isopropenylphenyl)methane (DDBM) and its polymer in CDCl$_3$.
a, Poly(DDBM). Polymerization conditions: [M]$_0$ = 0.06 mol dm^{-3}, [SnCl$_4$] = 1 mmol dm^{-3} in 1,2-dichloroethane for 15 min at 20°C.
b, DDBM.
Arrows show chemical shifts of three methyl groups in 1,1,3-trimethyl-3-phenylindan.

where ε_d and ε_i are molar extinction coefficients, and c_d and c_i the concentrations of double bond and indian unit respectively. The coefficients ε_d and ε_i were determined by using monomer (MSt–C_1–MSt) and 1,1,3-trimethyl-3-phenylindan as standards. The concentration c_d could be measured independently from the absorption at $1625\,cm^{-1}$.

In Figure 5, the NMR spectra of decadeuterobis(p-isopropenylphenyl)methane and its polymer are shown. The increased amount of light hydrogen in the polymer, whose peaks appeared at 8.3 to 9.3τ, was calculated to be 0.486 atom per monomer unit. One light hydrogen was expected for a monomer unit in **V**. The value is close to the indan content (ca. 40%) of polymers obtained at 20°C, which was obtained by IR spectroscopy. The NMR spectrum of the polymer showed three peaks for methyl groups. Two peaks at the higher field are assigned to be two kinds of methyl groups (–CD_2H) at C-1 position in **V**. The third peak is temporarily

(5)
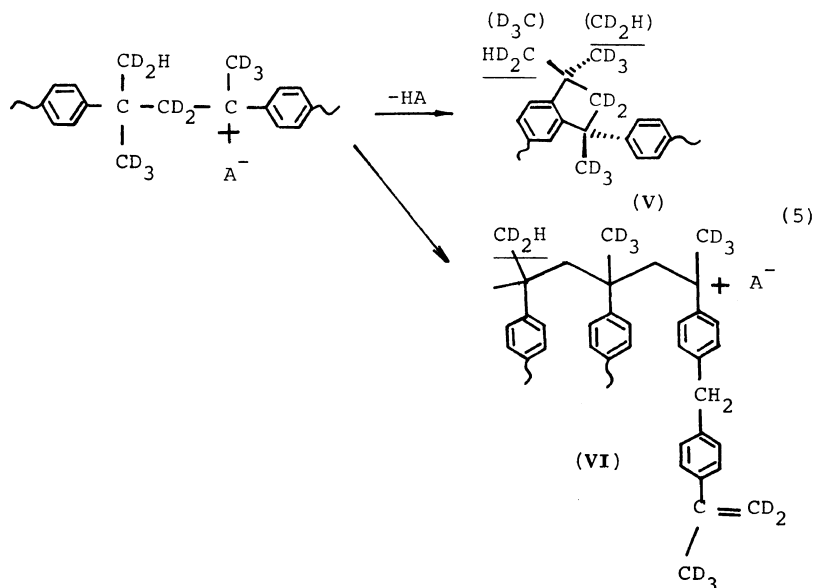
assigned to a methyl group (–CD_2H) in **VI**.

The unsaturated dimers of α-methylstyrene were formed in cationic conditions so that there could be the following two-step mechanism for the formation of indan units: the formation of unsaturated units, followed by the addition of proton and cyclization to the indan ring. However, the residual unsaturation in the polymer was almost always observed. The units (**III**) and/or (**IV**) should be detectable if they were formed, because it is unlikely that only the double bonds in units (**III**) and/or (**IV**) would react selectively. Therefore, the direct indan-ring formation is conceivable in the catalytic system.
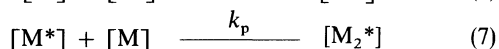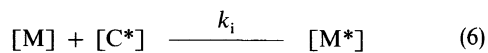
Dainton and Tomlinson concluded in their study of the polymerization of α-methylstyrene catalyzed by stannic chloride in ethyl chloride solution that chain transfer to monomer did not occur and that the rate of the proton-repulsion process involved in

chain termination was independent of both the catalyst and monomer concentrations.[10]

Moreover, it was observed that Friedel–Crafts benzylation was of third order: i.e., first order in Lewis acid, first order in benzyl chloride, and first order in aromatic compound.[11]

Therefore, it can be assumed that the indan-ring formation is the first order reaction of the appropriate active end and follows the regeneration of the catalyst.

Thus, the competition between transfer and propagation in the cationic polymerization of MSt–C_n–MSt can be expressed in the following equations

$$[M] + [C^*] \xrightarrow{\ k_i\ } [M^*] \tag{6}$$

$$[M^*] + [M] \xrightarrow{\ k_p\ } [M_2^*] \tag{7}$$

$$[M_2{}^*] + [M] \xrightarrow{\ k_p\ } [M_3{}^*] \tag{8}$$

$$\vdots$$

$$[M_{n-1}{}^*] + [M] \xrightarrow{\ k_p\ } [M_n{}^*] \tag{9}$$

$$[M_n{}^*] \xrightarrow{\ k_{tr}\ } [ID] + [C^*] \tag{10}$$

$$[M_n{}^*] \xrightarrow{\ k_t\ } [M_n] \tag{11}$$
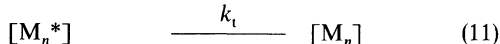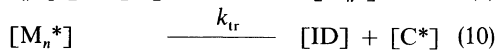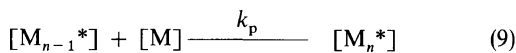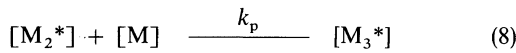
Where C^* is an active catalyst.

The rates are written as follows, if $k_t \ll k_{tr}$

$$-\frac{d[M]}{dt} = 2k_i[M][C^*] + 2k_p[M][M^*]$$
$$+ 2k_p[M][M_n{}^*] \tag{12}$$

$$\frac{d[M^*]}{dt} \cong 2k_i[M][C^*] - 2k_p[M^*][M] \tag{13}$$

$$\frac{d[M_n{}^*]}{dt} \cong 2k_p[M^*][M] - k_{tr}[M_n{}^*] \tag{14}$$

With the steady state approximation on $[M^*]$ and $[M_n{}^*]$ the following equations are obtained.

$$-\frac{d[M]}{dt} = 4k_i[M][C^*]$$
$$+ \frac{4k_ik_p}{k_{tr}}[M]^2[C^*] \tag{15}$$

$$\frac{d[ID]}{dt} = 2k_i[M][C^*] \tag{16}$$

When eq 15 is divided by eq 16,

$$-\frac{d[M]}{d[ID]} = 2 + \frac{2k_p}{k_{tr}}[M] \tag{17}$$

After the integration, the following equation is obtained

$$\frac{[ID]}{[M]_0 x} = \frac{r}{2[M]_0 x}$$
$$\times \ln\left[\frac{r + [M]_0}{r + [M]_0(1 - x)}\right] \tag{18}$$

$$r = k_{tr}/k_p \tag{19}$$

where $[ID]$, $[M]_0$, and x are the indan unit concentration, the initial monomer concentration, and the conversion, respectively.

As presented in Table II, the ratio k_{tr}/k_p obtained by using eq 18 was almost constant, even if the initial monomer concentration was changed from 0.06 to 0.12 mol dm^{-3}.

The polymerization of MSt–C_1–MSt was carried out at -21, 0, 10, and 20°C. The results are summarized in Table III. When the polymerization was carried out at a higher temperature, a larger k_{tr}/k_p value was obtained and the overall rate of polymerization became slower.

The cocatalytic activity of water in the cationic polymerization is well known.[12,13] The polymerization was carried out under a purified nitrogen atmosphere, so that the cocatalytic action of traces of water remaining in the system could be possible. However, as far as the data showed, the polymerization was carried out at least within a region of the $[H_2O]/[SnCl_4]$ ratio where the ratio did not affect

Table II. Effect of the initial monomer concentration on the transfer reaction[a]

$[M]_0$	$[C]$	Yield	ID[b]	DB[c]	k_{tr}/k_p
mol dm^{-3}	mmol dm^{-3}	%	%	%	mol dm^{-3}
0.06	1	42.9	38.0	23.3	0.15
0.08	1.3	83.7	36.8	8.3	0.12
0.10	1.6	67.6	33.9	18.6	0.14
0.12	2	72.7	32.4	19.0	0.13

[a] Polymerization conditions: monomer, MSt–C_1–MSt; solvent, CH_2Cl_2; catalyst, $SnCl_4$; temp, 20°C.
[b] The indan unit content.
[c] The content of residual unsaturation.

Table III. Polymerization of $MSt-C_1-MSt$ by stannic chloride at various temperatures[a]

Temp	Time	Yield	ID[b]	DB[c]	k_{tr}/k_p	Av
°C	min	%	%	%	$mol\,dm^{-3}$	
-21	1	53.5	9.6	82.4	0.010	
	2	71.9	12.9	8.6	0.012	0.011
0	1	40.0	27.9	41.0	0.060	
	2	47.4	27.9	34.3	0.057	
	3	62.9	32.6	25.3	0.075	0.065
	4	65.2	30.7	21.7	0.062	
10	2	29.3	33.3	37.9	0.10	
	3	48.2	38.5	28.8	0.15	0.13
	4	59.2	38.8	24.3	0.14	
20	3	35.6	39.9	31.3	0.19	
	4	42.9	38.0	23.3	0.15	0.17
	5	50.0	39.6	21.7	0.17	

[a] Polymerization conditions: $[M]_0$, $0.06\,mol\,dm^{-3}$; [C], $1\,mmol\,dm^{-3}$; solvent, CH_2Cl_2.
[b] The indan unit content.
[c] The content of residual unsaturation.

drastically the selectivity of the active site.

An Arrhenius plot of average values of k_{tr}/k_p showed that the ratio of the frequency factors (A_{tr}/A_p) was $6.6 \times 10^5\,mol\,dm^{-3}$ and the difference of activation energies $(\Delta E_{tr} - \Delta E_p)$ was $8.8\,kcal\,mol^{-1}$ $(36.8\;kJ\,mol^{-1})$. According to Dainton and Tomlinson,[10] $(\Delta E_{tr} - \Delta E_p)$ and A_p/A_{tr} were reported to be $4.5\,kcal\,mol^{-1}$ $(18.8\,kJ\,mol^{-1})$ and 1.2×10^{-3} $dm^3\,mol^{-1}$, respectively, in the polymerization of α-methylstyrene catalyzed by stannic chloride in ethyl chloride solution. These values were calculated from the average degree of polymerization by considering that all the saturated ends would be indan groups. Although we could not compare directly our data with their results because the monomers were not entirely the same, k_{tr}/k_p values of both polymerizations at 20°C were of the same order.

In conclusion, it was confirmed that $MSt-C_3-MSt$, a derivative of α-methylstyrene, did not cyclopolymerize by means of an acid-catalyst. The unusual behavior of $St-C_3-St$ in cyclopolymerization was again recognized. The transfer constant, k_{tr}/k_p, in the polymerization of $MSt-C_1-MSt$ could be calculated from the content of indan units in the polymer, which was determined directly by IR spectroscopy.

REFERENCES

1. Yu. V. Mitin and N. A. Glukhov, *Dokl. Akad. Nauk SSSR*, **115**, 97 (1957).
2. Yu. V. Mitin, *Vysokomol. Soedin.*, **6**, 484 (1964).
3. Yu. V. Mitin and T. D. D'yachenko, *Zh. Obsch. Khim.*, **34**, 1108 (1964).
4. J. Furukawa and J. Nishimura, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 85 (1976).
5. J. Furukawa and J. Nishimura, *J. Polym. Sci., Polym. Symp.*, No. 56, 437 (1976).
6. A. Weisserberger, E. P. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents," Interscience, New York, N. Y., 1957.
7. Yu. V. Mitin, *Zh. Obsch. Khim.*, **28**, 3302 (1958).
8. K. Matsuzaki, T. Uryü, K. Osada, and T. Kawamura, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2873 (1974).
9. D. J. Worsfold and S. Bywater, *J. Am. Chem. Soc.*, **79**, 4917 (1957).
10. F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).
11. H. C. Brown, H. W. Pearsall, L. P. Eddy, W. L. Wallace, M. Grayson, and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).
12. For a review, see A. R. Mathieson, "The Chemistry of Cationic Polymerization," P. H. Plesch Ed., Pergamon Press, London, 1963, Chapter 6.
13. For a review, see S. Bywater, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., Pergamon Press, London, 1963, Chapter 7.