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The Spontaneous Copolymerization of Indene with Polar Vinyl Monomers in the Presence of Zinc Chloride

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ABSTRACT

Indene (ID) was found to copolymerize spontaneously with polar vinyl monomers containing a nitrile or ester group in the presence of $ZnCl_2$ and to give rise simultaneously to its cationic homopolymer in the latter comonomer. The formation of a 1:1-charge transfer complex between ID with acrylonitrile coordinated to $ZnCl_2$ ((AN)c) was confirmed by UV-spectroscopic studies and the equilibrium constant for it was estimated to be 0.121 L/mol in AN at 25°C. The overall activation energy for the copolymerization with (AN)c was obtained to be ~9.8 kcal/mol. An increasing amount of $ZnCl_2$ in AN resulted in increases in the copolymerization rate, viscosity, and alternating tendency of the copolymer. The addition of 1,1-diphenyl-2-picrylhydrazyl to the system ID-(AN)c retarded the copolymerization and induced a cationic polymerization of ID. Further, terpolymers containing ~50 mol % AN were formed spontaneously in the system ID-styrene-(AN)c. Comparing these results with the corresponding ones obtained for 1,3-cyclodienes as donor monomer reported previously, a discussion is given on the reactivity of ID-(AN)c complex in the initiation and the propagation of the copolymerization. The mechanism of the attendant cationic polymerization of ID is briefly considered.

INTRODUCTION

Polar vinyl monomers complexed with Lewis acids have been known to copolymerize with electron-donating monomers to give rise to alternating copolymers [1-6]. Especially in the system involving styrene (St) and acrylonitrile (AN) in the presence of $ZnCl_2$, copolymerization has been found to take place spontaneously [1, 2] and it has been suggested to be initiated by radicals derived from the charge-transfer (CT) complex between St and AN coordinated to $ZnCl_2$ [1, 3]. It has previously been reported that 1,3-cyclodienes of six- to eight-membered rings also undergo a spontaneous copolymerization, although accompanied by cycloaddition for 1,3-cyclohexadiene (1,3-CHD) and 1,3-cycloheptadiene (1,3-CHpD) as dienes, with AN in the presence of $ZnCl_2$, while only cycloaddition occurs in the system involving cyclopentadiene as a diene [7-10].

On the other hand, it has been also shown that spontaneous copolymerization is accompanied by a cationic polymerization of donor monomers in the systems containing St and methyl methacrylate (MMA) in the presence of $ZnCl_2$ [2], and α-methylstyrene and AN in the presence of ethylaluminum sesquichloride (EASC) [11]. Moreover, only a cationic homopolymer is formed in the reaction of 1,3-CHD with MMA coordinated to $ZnCl_2$ [12].

Indene (ID) has a cyclopentadiene ring fused with a benzene ring and a higher electron-donating ability than those of 1,3-cyclodienes and St [13]. So far, alternating copolymers have been prepared in the copolymerization of ID with AN [14], methyl acrylate (MA), and MMA [15] in the presence of EASC. However, the copolymerization of ID with polar vinyl monomers in the presence of $ZnCl_2$ has not yet been reported in detail.

In the present study the copolymerizability of ID with polar vinyl monomers, mainly AN, coordinated to $ZnCl_2$ was investigated and it was compared with those obtained when 1,3-cyclodienes were used as donor monomers. Indene was found to copolymerize spontaneously with all the acceptor monomers used, in the presence of $ZnCl_2$, and further, an attendant formation of a cationic homopolymer of ID was observed in the copolymerizations with AN coordinated to $ZnCl_2$ in the presence of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as a radical scavenger and with MA or MMA in the presence of $ZnCl_2$. Such a cationic polymerization of ID is briefly discussed.

EXPERIMENTAL

Materials

Indene (Wako Pure Chemicals Industries) was treated with active carbon, dried with CaH_2, and then distilled under reduced pressure before use. Polar vinyl monomers were purified in the usual manner after dehydration with P_2O_5 (for AN, methacrylonitrile (MAN) and α-chloroacrylonitrile (CAN) and with CaH_2 (for MA, MMA, and methyl α-chloroacrylate (MCA)). $ZnCl_2$, guaranteed reagent grade, was dried in the melt under vacuum prior to use.

Spectral Measurements

UV spectra were obtained with a Shimadzu UV-180 spectrophotometer in an excess of AN as a solvent at 25°C. Quartz cells of 1 cm path length were used. IR and NMR spectra were determined on Shimadzu IR-400 and Hitachi R-24B spectrometers, respectively.

Copolymerization

The copolymerization was carried out in a reaction tube (~15 mL) with a stopcock under a nitrogen atmosphere. The copolymerization under UV irradiation was conducted in a quartz tube (~15 mL). The UV light was supplied by a high-pressure mercury lamp of 400 W.

The mixed solution prepared by dissolving $ZnCl_2$ in an excess of polar vinyl monomers was introduced into the reaction tube. ID (mixture of ID and St in the terpolymerization) was added to this solution by means of a syringe. DPPH was added prior to injecting ID. After mixing thoroughly, the reaction tube was then inserted in a fixed temperature bath. The copolymerization was stopped by pouring the reaction mixture into an acidified methanol. The product was extracted with cyclohexane to fractionate into an insoluble portion (copolymer) and a soluble one (homopolymer of ID). These products were evidenced by IR, NMR, and elemental analysis.

Analyses

The composition of copolymer and terpolymer was determined by elemental analysis as well as by IR and NMR spectra. IR and NMR spectra were used to determine the proportion of ID and St in the terpolymer. The viscosity of the copolymer was measured at a concentration of 0.5 g/dL in nitrobenzene (for the copolymer containing AN or MAN) or in methyl ethyl ketone (for that containing CAN, MA, MMA, or MCA) at 25°C by the use of a Ubbelohde viscometer.

RESULTS

Charge-Transfer Complex of ID with AN Coordinated to $ZnCl_2$

Figure 1 shows UV-spectra for an AN coordinated to $ZnCl_2$ ((AN)c), ID, and an equimolar mixture of ID and (AN)c in an excess AN. Under

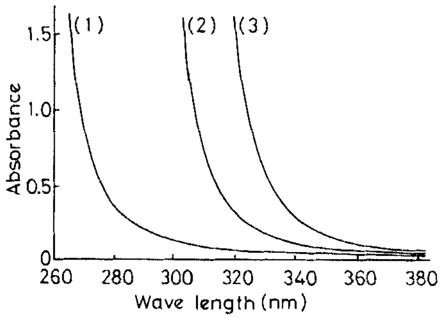

FIG. 1. UV absorption spectra of ID-(AN)c CT-complex and its components in AN as a solvent at 25°C. (1) [(AN)c] = 0.50 mol/L; (2) [ID] = 0.50 mol/L; and (3) equimolar mixture of ID and (AN)c, [ID] = [(AN)c] = 0.50 mol/L.

the present conditions the molar ratio of AN to $ZnCl_2$ is more than 5 and hence all the dissolved $ZnCl_2$ is assumed to be present in the form of $(AN)_2ZnCl_2$.

As seen in Fig. 1, the absorption of the mixed solution is profoundly enhanced in comparison with those of both components. This enhancement of the absorption can be attributed to the formation of a CT complex of ID with (AN)c.

As illustrated in Fig. 2, continuous variation plots of this CT band show maxima at the molar ratio of ID/(AN)c = 1/1, indicating that the CT complex is composed of an equimolar ID and (AN)c:

$$\text{ID} + (\text{AN})\text{c} \xrightleftharpoons{K_{CT}} \text{CT complex} \qquad (1)$$

The values of the equilibrium constant (K_{CT}) in Eq. (1), estimated by the method of Ketelaar et al. [16], are summarized in Table 1. The K_{CT} value for the present system is larger than those obtained for 1,3-cyclodienes of 6- to 8-membered ring [10] or St-AN-$ZnCl_2$ [2] systems.

Copolymerization of ID with AN in the Presence of $ZnCl_2$

The results of the copolymerization of ID with AN under various conditions are shown in Table 2. ID copolymerizes spontaneously with AN at a considerable rate in the presence of $ZnCl_2$ to yield a copolymer with a higher viscosity and alternating property than that

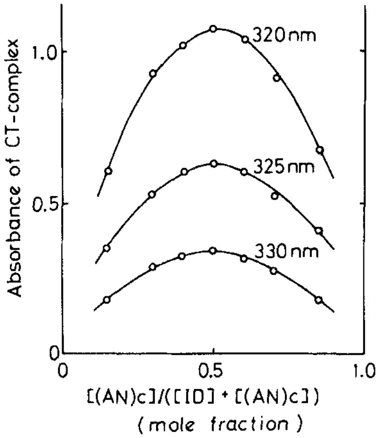

FIG. 2. Continuous variation plots for ID-(AN)c CT-complex in AN as a solvent at 25°C. ([ID] + [(AN)c]) = 1.00 mol/L.

TABLE 1. Equilibrium Constant (K_{CT}) and Molar Absorption Coefficient (ϵ_{CT}) of ID-(AN)c CT Complex in AN at 25°C[a]

Wavelength (nm)		K_{CT} (L/mol)	ϵ_{CT} (L/mol cm)
320		0.111	71.4
325		0.120	38.5
330		0.133	23.8
	Average	0.121	

[a] [ID] = 0.051 mol/L. The concentration of (AN)c was varied from 1.25 to 5.00 mol/L.

obtained by AIBN (α,α'-azobisisobutyronitrile) initiated copolymerization in the absence of $ZnCl_2$. The addition of DPPH as a radical scavenger retards the copolymerization and gives rise to a product with AN content of less than 50 mol% owing to a concurrent formation of ID homopolymer, as described later. The copolymerization of ID with a 1:1 complex of AN with $ZnCl_2$ results in an alternating copolymer.

The influence of reaction temperature on copolymerization is presented in Fig. 3. The rate of copolymerization is rapid in the initial period of reaction time and falls later. The overall activation energy

TABLE 2. Copolymerization of ID with AN[a]

Run no.	ID/AN/$ZnCl_2$ in feed (molar ratio)	Additive (mol% to ID)	Temperature (°C)	Copolymer		
				Yield[b] (%)	η_{sp}/C[c] (dL/g)	AN content (mol%)
01	1/5/1		50	25.0	0.76	56.9
02	1/5/0		"	3.2	0.24	64.6
03	1/5/0	AIBN,[d] 2.0	"	41.8	0.20	74.0
04	1/5/1		40	16.0	0.78	55.4
05	1/5/1	DPPH,[e] 0.5	"	1.5	-	40.9
06[f]	1/1/1	Sulfolane, 4 mL	"	16.6	0.64	49.8
07[g]	1/2/1	Sulfolane, 4 mL	"	20.6	0.71	52.5

[a] Feed: ID = 10.0 mmol; reaction time, 24 h.
[b] Calculated on basis of total monomer charged.
[c] Determined in nitrobenzene, C = 0.5 g/dL at 25°C.
[d] α,α'-Azobisisobutyronitrile.
[e] 1,1-Diphenyl-2-picrylhydrazyl.
[f] Solution of AN·$ZnCl_2$ (1:1) complex in sulfolane as solvent was used.
[g] Solution of $(AN)_2$·$ZnCl_2$ (2:1) complex in sulfolane as solvent was used.

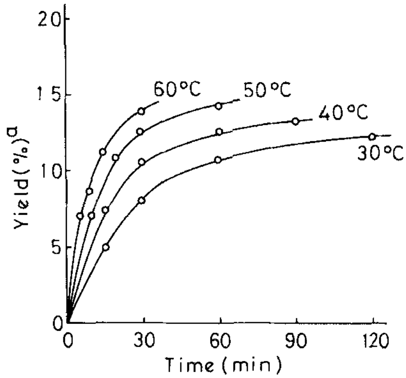

FIG. 3. Temperature effect on the copolymerization of ID with AN in the presence of $ZnCl_2$. Feed: ID = 10.0 mmol; ID/AN/$ZnCl_2$ (molar ratio) = 1/5/1. [a]Calculated as 1:1 copolymer.

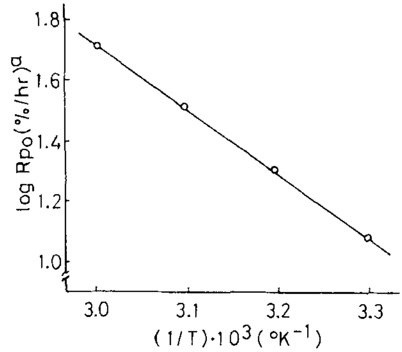

FIG. 4. Arrhenius plot for the copolymerization of ID with AN in the presence of $ZnCl_2$. Conditions as shown in Fig. 3. [a]Apparent initial rate of copolymerization.

for the copolymerization was found to be ~9.8 kcal/mol from the Arrhenius plot, illustrated in Fig. 4, with respect to the apparent initial rate of copolymerization estimated from the curves in Fig. 3. This value is relatively lower than those obtained for the copolymerization of 1,3-cyclodienes of 6- to 8-membered rings with AN in the presence of $ZnCl_2$ under similar conditions [7-9].

As shown in Fig. 5, increasing $ZnCl_2$ concentration results in increases in the rate of copolymerization, the viscosity, and the alternating tendency of the copolymer. Such dependences of the

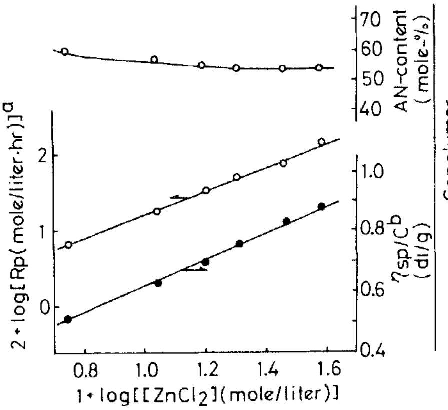

FIG. 5. Effect of $ZnCl_2$ concentration on the copolymerization of ID with AN in the presence of $ZnCl_2$. Feed: [ID] = 1.95 mol/L in AN. Temperature: 40°C. ^{a}Rate of copolymerization. ^{b}Determined in nitrobenzene, C = 0.5 g/dL at 25°C.

copolymerization characteristics on $ZnCl_2$ concentration are about the same for the copolymerization of 1,3-CHpD with AN in the presence of $ZnCl_2$ [8], except the AN content of copolymer, as a whole, is slightly higher than that for the latter system and they can be interpreted by considering the alteration in the concentrations of the CT complex, (AN)c, and free AN with $ZnCl_2$ concentration, as described in the previous paper [8]. The deviation of the copolymer composition from an alternating one can be attributed to additional participations of (AN)c and free AN in the propagation proceeding through the CT-complex and little dependence of the copolymer composition on $ZnCl_2$ concentration in the range of higher $ZnCl_2$ concentration seems to result from a preferential participation of (AN)c rather than free AN in the propagation. Thus the lower alternating tendency of the ID-AN copolymer compared to that of 1,3-CHpD-AN copolymer is ascribable to the lower reactivity of the CT complex of ID with (AN)c, as will also be referred to in the section on terpolymerization.

As shown in Table 3, the addition of DPPH retards the copolymerization while it induces the formation of ID homopolymer, which increases with an increasing amount of DPPH. The IR spectrum of the resulting ID homopolymer repeatedly reprecipitated shows no peak due to a nitrile group but peaks at 1335 and 1540 cm^{-1}, as illustrated in Fig. 6. These bands can be assigned to a nitro group, indicative of the presence of DPPH, presumably combined at the polymer chain end. Thus no incorporation of AN into ID homopolymer is ascribable to a cationic polymerization of ID.

The copolymerization under UV irradiation is profoundly accelerated,

TABLE 3. Effect of 1,1-Diphenyl-2-picrylhydrazyl (DPPH) on the Reaction of ID with AN in the Presence of $ZnCl_2$[a]

Run no.	DPPH (mol% to ID)	Yield (%)	
		Copolymer[b]	Polyindene[c]
04	0	36.1	0
08	0.5	1.4	3.1
09	1.0	0.8	5.3
10	5.0	0	15.6

[a] Feed: ID = 10.0 mmol, ID/AN/$ZnCl_2$ (molar ratio) = 1/5/1. Temperature: 40°C. Time: 24 h.

[b] Calculated as 1:1 copolymer.

[c] Calculated on basis of ID charged.

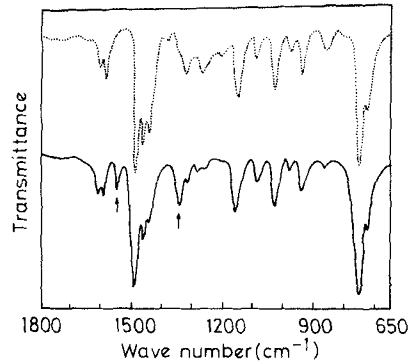

FIG. 6. IR spectra of ID homopolymers obtained (•••) in a cationic polymerization (BF_3OEt_2 as an initiator was used) and (—) in the copolymerization of ID-AN-$ZnCl_2$ system in the presence of DPPH.

as depicted in Fig. 7. This effect can be attributed to an increase in the contribution of the dative structure, responsible for the initiation of the copolymerization, in the CT complex. In this case the copolymer obtained under UV irradiation is slightly enriched in AN, presumably because of an enhanced reactivity of free AN caused by UV irradiation.

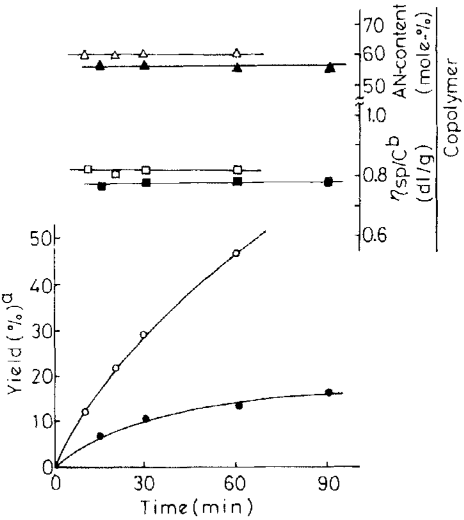

FIG. 7. Effect of UV irradiation on the copolymerization of ID with AN in the presence of $ZnCl_2$. Feed: ID = 10.0 mmol; ID/AN/$ZnCl_2$ (molar ratio) = 1/5/1. Temperature: 40°C. (○, □, △): Under UV irradiation; (●, ■, ▲): in dark. ^{a}Calculated as 1:1 copolymer. ^{b}Determined in nitrobenzene, C = 0.5 g/dL at 25°C.

Copolymerization of ID with Other Polar Vinyl Monomers in the Presence of $ZnCl_2$

The results of the copolymerization of ID with polar vinyl monomers other than AN in the presence of $ZnCl_2$ are given in Table 4. Similarly, a spontaneous copolymerization takes place for all the systems containing polar vinyl monomers with a nitrile or ester group, but it is accompanied by the formation of ID homopolymer for the latter system in the presence of $ZnCl_2$. The incorporation of an MA or MMA unit into the resulting ID homopolymer was not confirmed by IR and NMR spectra.

The copolymerizability of polar vinyl monomers with respect to the yield and the alternating tendency of the copolymer is in the following order: CAN > AN > MAN and MA > MMA. The copolymerization with MCA proceeds at a considerable rate even in the absence of $ZnCl_2$. Therefore the copolymerizability of MCA is presumed to be higher than that of MA, although the copolymerization in the presence of $ZnCl_2$ could not be carried out owing to the polymerization of MCA during dissolution of $ZnCl_2$ in it. Such a copolymerizability of polar vinyl monomers corresponds to their e value [17] in each homologous series, i.e., electron-accepting ability, because CT complexes of ID

TABLE 4. Copolymerization of ID with Polar Vinyl Monomers (PVM) in the Presence of $ZnCl_2$[a]

				Yield		Copolymer	
Run no.	PVM[b]	Q[c]	e[c]	Copolymer[d] (%)	Polyindene[e] (%)	η_{sp}/C[f] (dL/g)	PVM content (mol%)
11[g]	CAN	2.16	1.48	4.5	0	0.30	52.1
12	"	"	"	28.2	0	0.49	49.8
13	MAN	1.12	0.81	3.9	0	0.46	67.3
14[g]	MCA	2.02	0.77	10.1	0	0.25	71.9
15	MA	0.42	0.60	10.9	8.7	0.37	62.5
16	MMA	0.74	0.40	8.5	4.6	0.48	85.5
17	EA	-	-	-	0.2	-	-

[a] Feed: ID = 10.0 mmol, ID/PVM/$ZnCl_2$ (molar ratio) = 1/5/1. Temperature: 40°C. Time: 24 h.

[b] CAN: α-chloroacrylonitrile; MAN: methacrylonitrile; MCA: methyl α-chloroacrylate; MA: methyl acrylate; MMA: methyl methacrylate; EA: ethyl acetate.

[c] L. J. Young, Polymer Handbook, 2nd ed. (J. Brandrup and E. H. Immergut, eds.), Wiley, New York, 1975, p. II-387.

[d] Calculated on basis of total monomer charged.

[e] Calculated on basis of ID charged.

[f] Determined in methyl ethyl ketone (nitrobenzene for the copolymer containing MAN), C = 0.5 g/dL at 25°C.

[g] The run in the absence of $ZnCl_2$.

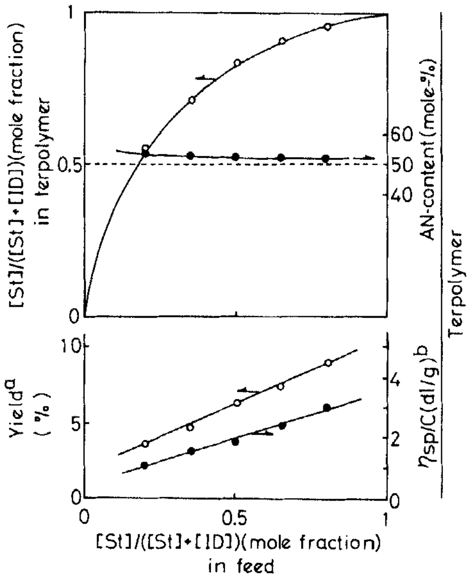

FIG. 8. Effect of feed composition of donor monomers in the terpolymerization of ID, St, and AN in the presence of $ZnCl_2$. Feed: [(ID + St)] = 2.92 mol/L. [$ZnCl_2$] = 1.46 mol/L in AN. Temperature: 40°C. Time: 1 h. [a]Calculated as the molar ratio of donor monomer to AN, (ID + St)/AN = 1/1, in the terpolymer. [b]Determined in nitrobenzene, C = 0.5 g/dL at 25°C. The curve representing the proportion of ID and St in the terpolymer is calculated for the apparent reactivity ratios of 0.23 and 5.1 for the ID-(AN)c and St-(AN)c complexes, respectively.

with polar vinyl monomers coordinated to $ZnCl_2$ are related both to the initiation and to the propagation of the copolymerization, as described in the section above. On the other hand, although a small amount of ID homopolymer is formed in ethyl acetate in the presence of $ZnCl_2$, the yield is enhanced in the system involving MA or MMA as a polar vinyl monomer. This indicates that the formation of ID homopolymer (a cationic polymerization) is also related to the CT complex of ID with MA or MMA coordinated to $ZnCl_2$, as suggested by Gaylord et al. [11].

Terpolymerization of ID, St, and AN in the Presence of $ZnCl_2$

The system involving ID, St, and AN in the presence of $ZnCl_2$ also undergoes a spontaneous terpolymerization to give rise to terpolymers forming a tough film. As shown in Fig. 8, increasing the feed composition of St, under the conditions ([ID] + [St]) = [(AN)c] = constant, results in increases in the yield and the viscosity of the terpolymer. The AN content in the terpolymer is close to 50 mol%, irrespective of the feed composition of the donor monomers. Therefore the present terpolymerization can be regarded as a binary copolymerization of the ID-(AN)c complex with the St-(AN)c complex, although some participation of (AN)c in the propagation has to be allowed because of a slight deviation from 50 mol% content of AN in the terpolymer. In this manner the apparent reactivity ratios of the ID-(AN)c complex and the St-(AN)c complex were estimated by a procedure similar to that shown by Ito et al. [18]: $r_{ID}(K_{ID}/K_{St}) = 0.23$ and $r_{St}(K_{St}/K_{ID}) = 5.1$, respectively; where K_{ID} and K_{St} are the K_{CT} values for the CT complexation of ID and St, respectively, with (AN)c in AN. This value of $r_{ID}(K_{ID}/K_{St})$ is smaller compared to the corresponding one for the 1,3-CHpD-(AN)c complex obtained in the terpolymerization of 1,3-CHpD, St, and AN in the presence of $ZnCl_2$ under similar conditions [19]. Such a reactivity of the ID-(AN)c complex based on the results of terpolymerization is compatible with that obtained for the copolymerization of ID with AN in the presence of $ZnCl_2$.

DISCUSSION

It has been thought so far that a spontaneous copolymerization of donor and acceptor monomers proceeds through the participation of the CT complex formed between comonomers both in the initiation and in the propagation of copolymerization [3, 20, 21]. From the results on the copolymerizations of ID and 1,3-cyclodienes with AN in the presence of $ZnCl_2$, it is confirmed that the overall activation energy for the copolymerization is decreased with an increase in the K_{CT} value for the CT complexation between donor monomer and (AN)c or in the electron-donating ability of the donor monomer [13]. Since an activation energy for the formation of initiating radicals is considered to comprise a large portion of the overall energy in a spontaneous copolymerization, the above relation indicates that the facility of formation of initiating radicals is determined to an extent by the contribution of the dative structure in the CT complex which is related to the K_{CT} value. This is compatible with the proposed mechanism [1, 20] that the initiating radicals are formed through the dative structure in the CT complex:

$$\mathrm{ID} + (\mathrm{AN})\mathrm{c} \overset{K_{CT}}{\rightleftharpoons} [\mathrm{ID} \rightarrow (\mathrm{AN})\mathrm{c} \longleftrightarrow \underset{\substack{\big\downarrow \\ \text{initiating} \\ \text{radicals}}}{\mathrm{ID}^{\overset{+}{\cdot}}(\mathrm{AN})\mathrm{c}^{\overset{-}{\cdot}}}] \qquad (2)$$

Thus the ID-(AN)c complex is more reactive for the formation of initiating radicals than the complexes of 1,3-cyclodienes with (AN)c.

On the other hand, the reactivity of the ID-(AN)c complex in propagation can be also drawn from the results of the composition of the resulting copolymer and terpolymer in the copolymerization of ID with AN and in the terpolymerization of these monomers with St, respectively, in the presence of $ZnCl_2$, and it was found to be lower than that of the 1,3-CHpD-(AN)c complex. This result implies that the reactivity of the CT complex is not always related to the K_{CT} value. In the ID-(AN)c complex the aromatic ring of ID, which does not participate directly in the propagation, is considered to be oriented around the (AN)c molecule from analogy to the conformation of the CT complex between St and MMA coordinated to $SnCl_4$ reported by Hirai et al. [22], while the 1,3-cyclodiene-(AN)c complex should assume the conformation in which the conjugated double bond of dienes is coordinated to the (AN)c molecule. Therefore, such a structural factor of the CT complex is presumably responsible for a relatively lower reactivity of the ID-(AN)c complex in spite of a large K_{CT} value. A detailed discussion on the relationship between the reactivity and the formation constant of the CT complex will be reported later.

Another finding in the present study is that the formation of ID homopolymer, i.e., a cationic polymerization of ID, takes place in the systems of ID, AN, and $ZnCl_2$ in the presence of DPPH, and along with a spontaneous copolymerization in the system of ID and MA or MMA in the presence of $ZnCl_2$. Such a cationic polymerization of ID is also related to the CT-complex, as already described in the present paper. The existence of a DPPH unit in the ID homopolymer formed in the former system is considered to result from a radical coupling between DPPH and the ID radical cation in the CT complex followed by cationic polymerization initiated by the resulting cationic species:

$$\begin{tikzcd}
\text{ID}^{+\cdot}(\text{AN})\text{c}^{-\cdot} \arrow[r] \arrow[dr, "\text{DPPH}"'] & \cdot\text{ID}(-\text{H}) + \cdot(\text{AN})\text{c}(+\text{H}) \arrow[r] & \text{radical copolymerization} \\
 & \text{DPPH-ID}^{+}(\text{AN})\text{c}^{-\cdot} \arrow[r] & \text{cationic polymerization}
\end{tikzcd}$$

Cationic polymerization of ID does not occur in the reaction with MCA in the absence of $ZnCl_2$, which gives rise to only copolymer with a considerable yield. Moreover, the yield of ID homopolymer is relatively low in ethyl acetate in the presence of $ZnCl_2$. Consequently, cationic polymerization of ID in MA or MMA in the presence of $ZnCl_2$ seems to be initiated by hydrogen abstraction from the radical anion of MA or MMA coordinated to $ZnCl_2$ in the CT complex (presumably from the methoxy group), and it occurs along with a spontaneous copolymerization initiated by proton transfer from a radical cation to a radical anion in the CT complex:

$$\begin{tikzcd}
\overset{+}{\mathrm{ID}}\cdot(\mathrm{MA})\mathrm{c}\overset{-}{\cdot} \arrow[r, "\text{proton transfer}"] \arrow[ddr, "\text{hydrogen transfer}"'] & \cdot\mathrm{ID(-H)} + \cdot(\mathrm{MA})\mathrm{c}(+\mathrm{H})\ (\text{or } \cdot(\mathrm{MMA})\mathrm{c}(+\mathrm{H})) \arrow[d] \\
(\text{or } (\mathrm{MMA})\mathrm{c}\overset{-}{\cdot}) & \text{radical copolymerization} \\
 & \mathrm{ID}^{+}(+\mathrm{H})(\mathrm{MA})\mathrm{c}\overset{-}{\cdot}\ (\text{or } (\mathrm{MMA})\mathrm{c}\overset{-}{\cdot}) \arrow[d] \\
 & \text{cationic polymerization}
\end{tikzcd}$$

where (MA)c and (MMA)c denote MA and MMA coordinated to $ZnCl_2$, respectively.

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