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Thermal Copolymerizations of Vinyl Sulfides with Some Weak Acceptor Monomers

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SUMMARY:

Thermal copolymerizations of vinyl sulfides (VS) with some weak electron-accepting monomers were studied on the basis of donor-acceptor interaction. VS were thermally polymerized in the presence of diethyl fumarate, dimethyl maleate, acrylonitrile (AN) methyl methacrylate, (MMA), methyl acrylate, and ethyl acrylate (EA) in the absence of radical initiators to yield copolymers. The monomer/copolymer composition curves for these copolymerizations were quite similar to those produced from polymerizations initiated by α,α' -azobisisobutyronitrile, indicating that the propagating species are free radicals. Similar conclusions were obtained from experiments with the inhibitor benzoquinone, and from the small observed solvent effect, but no proof for the occurrence of cationic or anionic polymerization was obtained.

Although the existence of a 1:1 donor/acceptor complex in AN/VS system was spectroscopically confirmed, such interaction was appreciably weak, in comparison to that of maleic anhydride/VS. In the systems MMA/VS and EA/VS no interaction was observed. Accordingly, the initiating radical species in AN/VS system might be considered to be formed through donor/acceptor interaction. It was also found that alternative copolymers were obtained from thermal copolymerization of AN with VS in the presence of zinc chloride. The initiation mechanism for these thermal copolymerizations is discussed.

ZUSAMMENFASSUNG:

Thermische Copolymerisationen von Vinylsulfiden (VS) mit einigen Monomeren mit schwachen Akzeptoreigenschaften wurden in bezug auf Donator-Akzeptor-Wechselwirkung untersucht. VS wurde thermisch in Gegenwart von Fumarsäureäthylester, Maleinsäuredimethylester, Acrylnitril (AN), Methacrylsäuremethylester (MMA), Acrylsäuremethylester und Acrylsäureäthylester (EA) und in Abwesenheit eines radikalischen Initiators zu Copolymeren umgesetzt. Die Kurven, die die Zusammensetzung an Monomeren und Copolymeren für diese Produkte wiedergeben, gleichen vollständig den Kurven von denjenigen Polymeren, die mit Azoisobuttersäuredinitril als Initiator erhalten werden, und weisen darauf hin, daß das Wachstum über freie Radikale verläuft. Eine ähnliche Schlußfolgerung wurde auch auf Grund der Inhibierung durch Benzochinon gezogen und auf Grund des geringen Lösungsmittelleffektes; es konnte jedoch keinerlei Nachweis für eine als Konkurrenzreaktion nebenher laufende kationische oder anionische Polymerisation erbracht werden.

Obleich bei dem AN/VS-System das Vorhandensein eines 1:1-Donator-Akzeptor-Komplexes spektroskopisch bestätigt werden konnte, ist solch eine Wechselwirkung im Vergleich mit der des Maleinsäureanhydrid/VS-Systems bemerkenswert schwach. Im Falle

von MMA/VS und EA/VS wurde eine derartige Wechselwirkung nicht beobachtet. Demgemäß kann man annehmen, daß sich die initiiierende Radikalform bei dem AN/VS-System auf dem Wege einer Donator-Akzeptor-Wechselwirkung bildet. Es wurde außerdem gefunden, daß sich ein entsprechendes Copolymeres aus der thermischen Copolymerisation von AN und VS in Gegenwart von Zinkchlorid bildet. Der Initiierungsmechanismus für diese thermischen Polymerisationen wird erörtert.

I. Introduction

In previous papers, it has been reported that vinyl sulfides (abbreviated as VS hereafter) can behave as typical electron-donating monomers¹⁻³, and readily undergo alternative copolymerization with strong electron-accepting monomer, *e.g.* maleic anhydride (MAN)⁴. This copolymerization occurred at moderate temperatures with a pale yellow colouration even in the absence of a radical initiator. Spectroscopic evidence suggested that the 1:1 charge transfer complex of VS with MAN had a small equilibrium constant of 0.090–0.035 l/mole in methylene chloride or chloroform at room temperature. Accordingly it is assumed that the initiating radical species in the alternative copolymerization, is produced from this complex which may also participate in the propagation step as well as both free monomers.

On the other hand, strong acceptor monomers other than MAN, such as sulfur dioxide⁵, have also been found to undergo alternative copolymerization with VS. The well-known strong organic acceptors, such as tetracyanoethylene, *p*-chloranil and tetracyanoquinodimethane, however, have not led to polymers or copolymers of VS⁶. This seems to arise from the fact that VS monomers have relatively high ionization potentials in comparison to N-vinylcarbazole (NVC), which can easily be polymerized by these organic acceptors⁷.

The thermal polymerization of N-vinyl monomers and vinyl ethers in the presence of weak acceptor monomers has been studied. ELLINGER⁷ has reported that N-vinylcarbazole (NVC), which has similar ALFREY-PRICE Q and *e* values as VS, can polymerize in the presence of relatively weak acceptor monomers, such as AN and methyl methacrylate (MMA), giving a homopolymer of NVC. He has also proposed that this polymerization is performed by a partial electron transfer (mesomeric polarization) mechanism, but not by an ordinary polymerization mechanism initiated by ion-radical species resulting from a complete electron transfer between both monomers.

However, ELLINGER⁸ rejected the formation of only homopolymer of NVC in the copolymerization of NVC with MMA; a copolymer of NVC

and MMA was obtained. Since anthracene retards the formation of the MMA copolymer, but does not markedly affect the formation of the NVC homopolymer, he considers that the homopolymerization of NVC proceeds through a mesomeric polarization mechanism.

TAZUKE and OKAMURA⁹⁾ investigated the thermal and photopolymerization of NVC with AN, in detail, and observed the simultaneous occurrence of cationic and radical polymerizations from the effects of additives, and interpreted the results in terms of polymerizations induced by ion-radical species, produced by donor-acceptor interaction. Furthermore, they have studied the thermal and photopolymerization of isobutyl vinyl ether (IBVE) with AN¹⁰⁾. Although the formation of the contact-charge transfer complex was confirmed, by electronic spectroscopy, the system was thermally stable at 50°C in the dark.

Generally thermal copolymerization of AN with donor monomers seems to be dependent on the ionization potential of the donor monomers employed. The ionization potential of the donor monomers decreases in the order: vinyl ether > vinyl sulfide > N-vinyl monomer, with slight variations depending on the substituent. Accordingly the thermal copolymerizability of VS with AN is expected to show intermediate behavior between N-vinyl monomer and vinyl ether.

In a previous paper¹⁾, VS was reported to copolymerize with AN, even in the absence of a radical initiator, and to show relatively high tendency to alternative copolymerization. Thus we report the thermal copolymerization of VS with AN and other weak acceptor monomers such as methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), dimethyl maleate (DMM) and diethyl fumarate (DEF) and discuss on the basis of spectroscopic evidence for the donor-acceptor interaction in these systems.

II. Experimental

II.1. Materials

Ethyl vinyl sulfide (EVS), isobutyl vinyl sulfide (IBVS) and phenyl vinyl sulfide (PVS) were prepared as described previously^{1,11)}. The other monomers, AN, MMA, MA, EA, DMM, DEF, and vinyl acetate (VAc) were purified from the commercial products by ordinary fractional distn. These monomers including VS were distd. just before use.

The commercial α,α' -azobisisobutyronitrile (AIBN) as radical initiator was twice recrystallized from ethanol. The solvents and the other reagents were purified by the usual methods.

II.2. Polymerization procedure

Copolymerization was carried out in sealed tubes, which were shaken in the absence of external light at 60°C. The required amounts of VS, comonomer and the other reagent were

charged into a hard glass tube, which was then degassed under *vac.* by conventional freezing and thawing techniques and sealed off under *vac.* This sealed tube was wrapped with aluminum foil to protect it from diffused light, and placed in a thermostat to start the polymerization.

After a given time, the tube was opened and its contents poured into a large amount of methanol to precipitate the copolymer. The copolymers with AN were then purified by reprecipitating it from dimethylformamide solution with excess methanol. For other copolymers, benzene was the solvent and methanol the precipitant. Conversions were calculated from the weight of the dried copolymer obtained.

II.3. Viscosity measurement

The reduced viscosities of the dilute solutions of copolymers were measured in an UBBELOHDE viscometer at 30°C. Dimethylformamide and benzene were used as solvents for AN copolymers and other copolymers, respectively.

II.4. Analyses of the copolymers

The composition of copolymers was determined by the elementary analyses of nitrogen and sulphur.

II.5. Spectroscopic measurement

For the measurement of the electronic spectra, a Hitachi EPS-2U spectrophotometer was used at room temp.

III. Results and Discussion

III.1. Thermal copolymerizations of VS with AN

In our previous paper¹⁾, we reported that IBVS and AN can undergo copolymerization in the absence of a radical initiator to give an almost alternating copolymer. Since homopolymerizations of both monomers do not occur, even at 60°C, this warranted a more detailed investigation.

Figs. 1–3 show the relationships of the composition (or yield and reduced viscosity) of the resulting copolymers of IBVS, EVS and PVS with AN, respectively, *versus* the monomer feed composition. The tendency to produce alternative copolymers in all systems, is high, although not as great as in the VS-MAN system.

The resulting monomer/copolymer composition curves shown in Figs. 1–3 are quite similar to those of polymers obtained from initiation by AIBN. Therefore the propagating species for these thermal copolymerizations seem to be free radicals. Similar conclusions can be drawn from the results shown in Tables 1 and 4, *i.e.* the thermal copolymerization is inhibited by benzoquinone and shows only small solvent effects (see Tables 1 and 4).

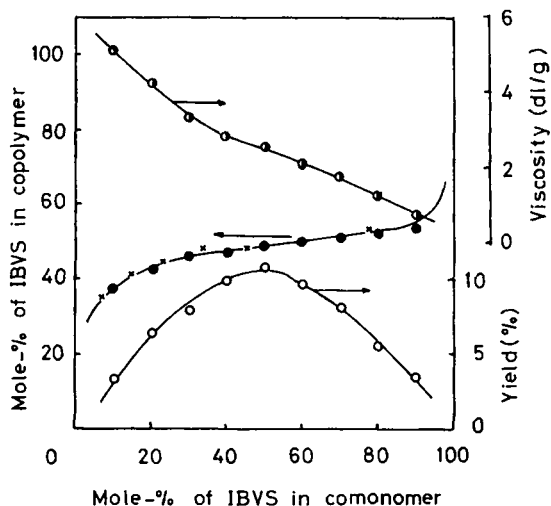


Fig. 1. Effect of the monomer composition on the yield (○), composition (●) and reduced viscosity (⊙) of the resulting copolymers in thermal copolymerization of IBVS (M_2) with AN (M_1) at 60°C for 30 min (Total monomers 50 mmole). The mark (x) in composition relation represents the results of AIBN-initiated copolymerization ($r_1 = 0.068$ and $r_2 = 0.050$)¹⁾, and reduced viscosity of a dimethylformamide solution (0.2 g/dl) is determined at 30°C

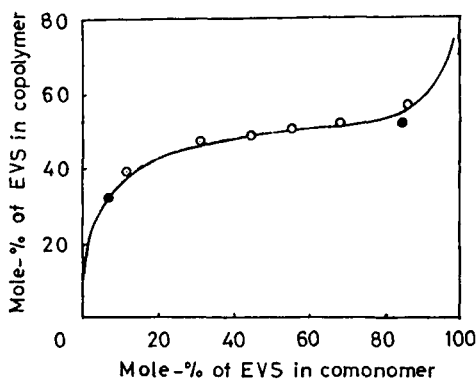


Fig. 2. Effect of the monomer composition on the composition of the resulting copolymers in copolymerization of EVS (M_2) with AN (M_1) at 60°C for 25 min (Total monomers 60 mmole). (○) indicate the results in the presence of AIBN ($r_1 = 0.065$ and $r_2 = 0.055$)¹⁾ and (●) in the absence of AIBN

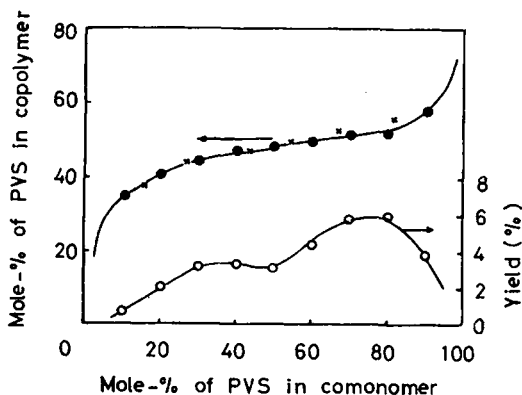


Fig. 3. Effect of the monomer composition on the yield (○) and composition (●) of the resulting copolymers in thermal copolymerization of PVS (M_2) with AN (M_1) at 60°C for 40 min (Total monomers 30 mmole). The mark (x) in composition relation represents the results of AIBN-initiated copolymerization ($r_1 = 0.11$ and $r_2 = 0.07$)¹⁾

The highest yield of the copolymer was produced at 1:1 molar composition of the monomer feed (see Fig. 1) and this is consistent with the case of VS/Man system, but the reduced viscosity of the resulting copolymers increases with increasing AN concentration. However, the AN/PVS system does not show the maximum yield at 1:1 monomer feed composition (see Fig. 3).

The time-conversion curves of the thermal copolymerization of AN with EVS, in which 1:1 molar monomer mixtures were used, are shown in Fig. 4. The thermal copolymerization begins at a relatively fast rate at moderate temperatures, and the reduced viscosities of the resulting copolymers are almost constant and independent of the conversion.

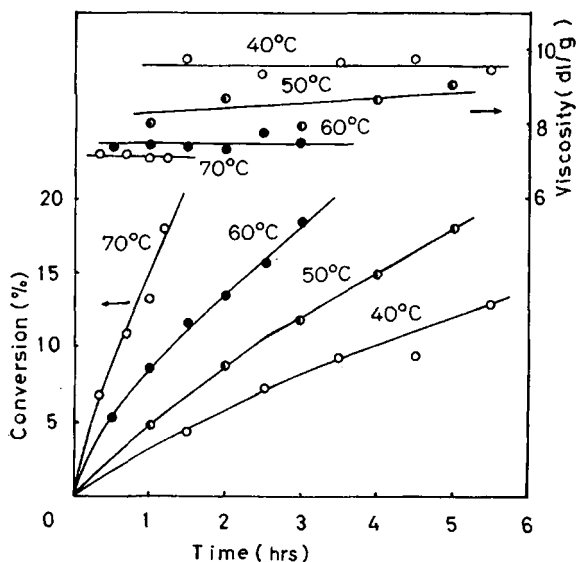


Fig. 4. Time-conversion and -reduced viscosity curves for thermal copolymerization of EVS (M_2) with AN (M_1) in benzene at 40–70°C. $[EVS] = 2.66$, $[AN] = 2.54$ mole/l.

The above results suggest that the initiating radical for this copolymerization is produced by a donor-acceptor interaction between AN and

Table 1. Effect of solvents on the copolymer yield in thermal copolymerization of AN with EVS at 60°C. $[AN] = [EVS] = 2.67$ mole/l., polymerization time: 35 min

Solvent	Yield (%)	Solvent	Yield (%)
None ^{a)}	26.5	Carbon tetrachloride	7.6
Benzene ^{b)}	8.3	Tetrahydrofuran	8.6
Toluene ^{b)}	8.7	Acetonitrile	8.7
<i>p</i> -Xylene ^{b)}	5.4	Dimethylsulfoxide	14.5

^{a)} $[AN] = [EVS] = 6.00$ mole/l.

^{b)} These copolymerizations proceeded heterogeneously.

VS. If such a donor-acceptor interaction is important to the initiation step, the rate of thermal copolymerization will be affected by the solvent employed. As shown in Table 1, however, π -donor solvents such as benzene do not appreciably affect the yield, although such solvents should weaken a π - π type interaction between VS and AN. Other solvents except dimethylsulfoxide did not also affect the copolymer yield. The solvent effect on the copolymer composition will also be described in section III.4.

III.2. Thermal copolymerizations of VS with other electron-accepting monomers

It is interesting to compare the rate of thermal initiation with the tendency to form alternative copolymers in copolymerizations of VS with various electron-accepting monomers. Table 2 summarizes the results of thermal copolymerizations of VS with MAn, DEF, DMM, AN, MMA, MA, and EA at 60°C. It is seen that all systems copolymerize even in the absence of radical initiator, but in contrast VS/MAN system⁴⁾, no colouration was observed.

Table 2. The results of thermal copolymerizations of IBVS (M_2) with various electron-accepting monomers (M_1) at 60°C

M_1	e_1 of M_1	Rate (%/hr) ^{a)}	r_1	r_2	$r_1 r_2$
MAn ^{b,c)}	2.25	54.0	~ 0	~ 0	~ 0
DEF	1.25	20.0	~ 0	~ 0	~ 0
DMM	1.27	0.4	0	0.2	0
AN ^{c)}	1.20	45.4	0.065	0.055	0.0036
EA	0.60	42.0	0.35	0.05	0.0175
MA	0.60	23.4	0.35	0.05	0.0175
MMA	0.40	3.8	0.94	0.04	0.0376

a) These represent the thermal rates at $[M_1] = [M_2] = 50$ mole-%.

b) From the previous results in benzene⁴⁾.

c) EVS was used as M_2 monomer.

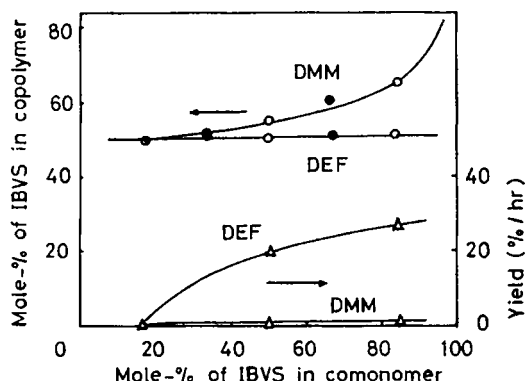


Fig. 5. Monomer/copolymer composition and yield curves for thermal copolymerizations of IBVS (M_2) with DMM (M_1) and of IBVS (M_2) with DEF (M_1) at 60°C (Total monomers 30 mmole). (O) polymerized in the presence of AIBN and (●) polymerized in the absence of AIBN ($r_1 = 0$ and $r_2 = 0.2$ for IBVS/DMM system). The mark (Δ) represents the yields of their copolymers

Fig. 5 shows the results of thermal copolymerization of DMM and DEF with IBVS. The rate of polymerization increases with increasing concentration of IBVS in monomer mixture. The copolymer composition curves were in agreement with those obtained when AIBN was the initiator. The resulting r_1 and r_2 values are given in Table 2.

For DEF/IBVS copolymerization system as well as the MAN/VS system, almost alternative copolymers were obtained with every monomer feed composition (Fig. 5). The rates of thermal copolymerization for the former system were much faster than those for the DMM/IBVS system. Thus the rate of thermal initiation is responsible for the alternating tendency. The difference between DMM and DEF is attributed to steric hindrance in the cross propagation step, as indicated by the ALFREY-PRICE Q values (DMM 0.09, DEF 0.61)¹³.

Figs. 6, 7 and 8 show the results of thermal copolymerization of VS with MMA, EA and MA, respectively. As can be seen from these figures, the thermal rates of polymerization for all systems reach a maximum at certain monomer compositions. The resulting copolymer composition curves for these three systems are in agreement with those obtained when AIBN was the initiator. These findings and the observed inhibition by benzoquinone indicate that these copolymerizations take place by a radical mechanism.

In Table 2, it is seen that the rates of thermal polymerization and the tendency to form alternative copolymers in copolymerization of IBVS with these different monomers (M_1), except DMM and DEF, are to some extent related to their e_1 values. Since the observed rates of thermal polymerization are not only attributable to the initiation rates, and since the mechanism of initiation is rather complex, as described in the next sections, a quantitative correlation between the rates of thermal polymerization and the tendency to form alternating copolymers is not possible.

III.3. *The existence of the interaction between AN and VS*

As described in the previous paper⁴), the formation of a 1:1 charge transfer complex of VS with MAN was confirmed by spectroscopy. The equilibrium constant for complex formation was relatively small.

VS has an appreciable tendency to copolymerize alternatively with AN. This may be explained in terms of the stabilization of the transition state of the cross propagation step, *i.e.* polar^{14,15} or charge transfer¹⁶ interaction between propagating radical and reacting monomer. However, a

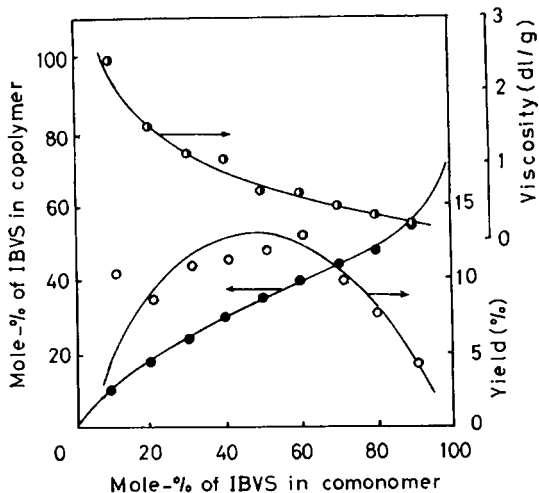


Fig. 6. Effect of the monomer composition on the yield (○), composition (●), and reduced viscosity (○) of the resulting copolymers in thermal copolymerization of IBVS (M_2) with MMA (M_1) at 60°C for 3 hrs (Total monomer 40 mmole). The solid line in composition relation represents the curve calculated as $r_1 = 0.94$ and $r_2 = 0.04^{11}$, and reduced viscosity was determined in benzene solution (0.2 g/dl) at 30°C

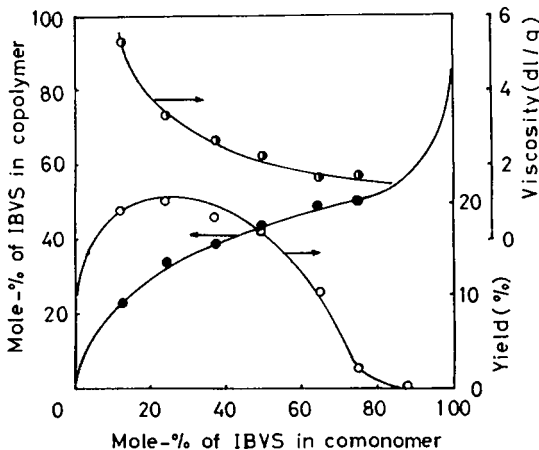


Fig. 7. Effect of the monomer composition on the yield (○), composition (●), and reduced viscosity (○) of the resulting copolymers in thermal copolymerization of IBVS (M_2) with EA (M_1) at 60°C for 25 min (Total monomers 40 mmole). The solid line in composition relation represents a curve calculated as $r_1 = 0.35$ and $r_2 = 0.05$, and reduced viscosity was obtained in benzene solution (0.2 g/dl) at 30°C

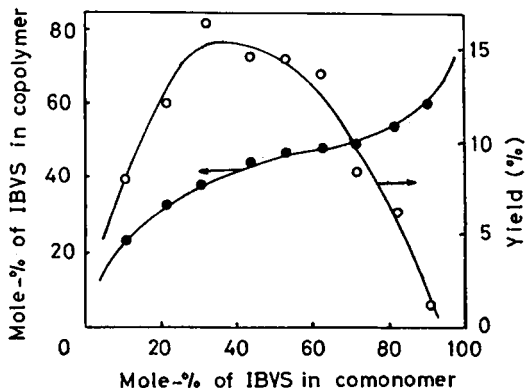


Fig. 8. Effect of the monomer composition on the yield (○) and composition (●) of the resulting copolymers in thermal copolymerization of IBVS (M_2) with MA (M_1) at 60°C for 35 min (Total monomers 30 mmole). The solid line in composition relation represents a curve calculated as $r_1 = 0.35$ and $r_2 = 0.05^{12}$

charge transfer complex formed between both monomers may also participate in the alternating copolymerization as stated by IWATSUKI *et al.* Accordingly, a spectroscopic study was necessary to prove this possibility, as shown for the MAn/VS system⁴⁾.

Figs. 9, 10 and 11 show the plots by continuous variation method of GARRETT and GUILLE¹⁷⁾ to determine the composition of the interaction between IBVS and weak acceptor monomers, AN, MMA and EA, respectively.

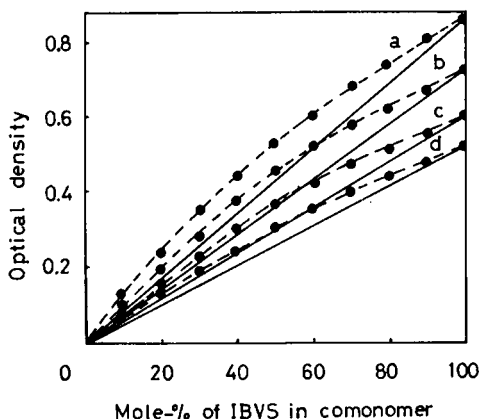


Fig. 9. Optical absorption of IBVS/AN system in *n*-heptane using 1 mm quartz cell: $([\text{IBVS}] + [\text{AN}]) = 1.95$ mole/l. a: 287 $\text{m}\mu$, b: 288 $\text{m}\mu$, c: 289 $\text{m}\mu$, d: 290 $\text{m}\mu$.

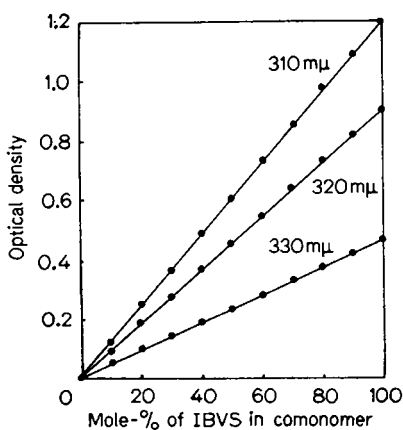


Fig. 10

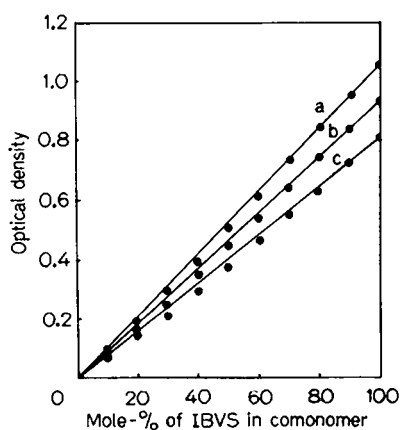


Fig. 11

Fig. 10. Optical absorption of IBVS/MMA system in *n*-heptane using 10 mm quartz cell: $([\text{IBVS}] + [\text{AN}]) = 1.00$ mole/l.

Fig. 11. Optical absorption of IBVS/EA system in *n*-heptane using 10 mm quartz cell: $([\text{IBVS}] + [\text{EA}]) = 1.00$ mole/l. a: 310 $\text{m}\mu$, b: 320 $\text{m}\mu$, c: 330 $\text{m}\mu$.

Although the measurements were carried out at high concentrations in *n*-heptane, using 1 and 10 mm quartz cells, the existence of some interaction between IBVS/EA and IBVS/MMA was not detectable within the range of wave length (270–340 $m\mu$) examined. For the IBVS/AN system, however, a deviation from a straight line expected from BEER's law was observed. Subtracting the absorption of each monomer from the observed absorption, a curve showing a maximum absorption at 1:1 molar composition is obtained. The result is shown in Fig. 12. This indicates the existence of 1:1 interaction.

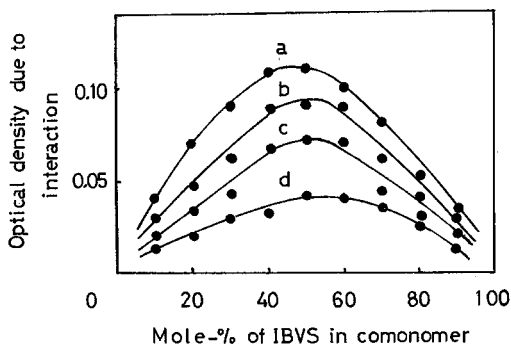


Fig. 12. Continuous variations of IBVS/AN system in *n*-heptane. Conditions are similar as Fig. 9

As expected, under the conditions used, the interaction between AN and VS is very weak, and is not considered to be complete. Similarly, TAZUKE and OKAMURA¹⁰ have proposed the formation of a contact-type charge transfer complex between AN and isobutyl vinyl ether.

Generally, in weak donor-acceptor interaction, the contribution due to VAN DER WAALS forces is considered to be greater than that of charge transfer¹⁸). This interaction observed spectroscopically reflects the change in electron energy between the donor and acceptor molecules, and accordingly the present result can not only be attributed to charge transfer. The polarization due to VAN DER WAALS forces seems to be the main interaction.

III.4. Solvent and dilution effects in the co- and terpolymerizations

A donor-acceptor interaction of AN/VS system is expected to be affected by the solvent employed, that is, the polarity and electron donating ability of the solvent may change the strength of this interaction. If this consideration is correct, the monomer reactivity ratios in the copolymerization will be changed by the solvent employed, and in the terpolymerization, in which the third monomer does not interact with the other

monomers, the dilution effect of the solvent on the resulting terpolymer composition will be observed. IWATSUKI *et al.*¹⁹⁾ have proposed that the observed dilution effect in some terpolymerization systems can be explained in terms of a complex propagating mechanism. They have observed large dilution effects by various solvents on the terpolymer composition in MAN/*p*-dioxene/AN and MAN/chloroethyl vinyl ether/AN systems, where AN is the third monomer.

Table 3 and Fig. 13 show the dilution effect of benzene on the terpolymer composition of the terpolymerization of EVS, AN and VAc at 60°C.

Table 3. Dilution effect of benzene on the terpolymer composition for AIBN-initiated terpolymerization of AN, EVS, and VAc at 60°C. [AIBN] = $1.1 \cdot 10^{-3}$ mole; Monomer composition: total monomers 45.6 mmole, [AN] = 23.7, [EVS] = 22.8, [VAc] = 53.5 mole-%

No.	Benzene (ml)	Time (min)	Conv. (%)	Terpolymers obtained (mole-%)				
				N (%)	S (%)	[EVS]	[AN]	[VAc]
1	0	20	12.3	9.69	19.40	42.8	49.0	8.2
2	0.5	20	10.3	10.15	18.17	40.9	50.8	8.3
3	1	20	8.3	10.18	20.17	44.1	51.0	4.9
4	2	40	15.3	9.97	20.69	45.3	49.9	4.8
5	3	40	11.0	10.14	20.14	44.1	50.8	5.1
6	4	65	14.2	10.09	19.34	41.9	50.1	7.0
7	5	65	11.4	9.59	19.00	42.0	48.5	9.5
8	10	100	4.0	9.78	19.45	42.7	49.1	8.2
9	14	115	11.0	9.76	19.06	42.1	49.3	8.6

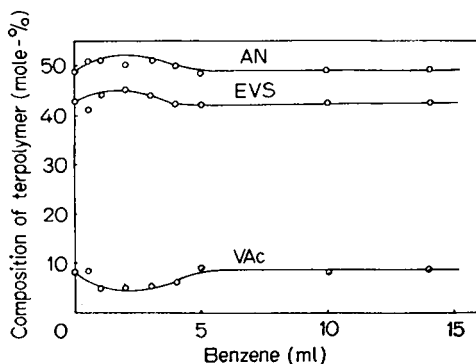


Fig. 13. Dilution effect of benzene on the terpolymer composition in EVS/AN/VAc terpolymerization at 60°C. [AIBN] = $1.1 \cdot 10^{-3}$ mole. Total monomers = 45.6 mmole, [EVS] = 22.8, [AN] = 23.7, [VAc] = 53.5 mole-%

From Table 3, the maximum change in composition of the terpolymers by the addition of benzene solvent is found to be about 5 mole-% with respect to VAc unit.

Although this terpolymerization proceeds heterogeneously, the composition of the resulting terpolymers was generally unaffected by the heterogeneity of the system, unless specific interaction (*e.g.* selective adsorption *etc.*) between the propagating radical and monomer occurred. The dilution effect in the terpolymerization containing MAN has been observed to be independent of the heterogeneity of the system¹⁹). Accordingly, the heterogeneity of this polymerization system might not affect the terpolymer composition. Since a difference in composition was observed on dilution, a donor-acceptor interaction is indicated.

The effect of solvents employed on the copolymer composition in the copolymerization of AN with EVS at 60°C is shown in Table 4. A very slight solvent effect was observed. Although a complete explanation of these solvent and dilution effects is not possible, electron donating solvents such as benzene would weaken the interaction between AN and VS, while the interaction between benzene and AN increases. Hence one of the explanations for these solvent effects is to consider an interaction between a propagating AN radical and benzene, leading to a decrease in the reactivity of the AN radical. As shown in Table 4, the observed difference in composition of the copolymerization in benzene and carbon tetrachloride seems to suggest this concept.

Table 4. Effect of solvent on the copolymer composition for thermal copolymerization of AN and EVS at 60°C. Total monomer 4 ml, solvent 2 ml; polymerization time 25 min

Solvent	Monomer feed ([EVS] = 84.9 mole-%)			Monomer feed ([EVS] = 6.9 mole-%)		
	Yield (%)	N (%) of copolymer	[EVS] (mole-%) in copolymer	Yield (%)	N (%) of copolymer	[EVS] (mole-%) in copolymer
None	4.5	9.33	52.4	1.4	14.44	33.3
Benzene ^{a)}	2.7	9.84	50.3	0.6	14.37	33.5
Toluene ^{a)}	2.4	9.27	52.6	0.8	14.19	34.1
<i>p</i> -Xylene ^{a)}	2.1	9.40	52.2	0.7	14.33	33.7
Carbon tetrachloride	1.6	8.79	54.7	0.7	14.04	34.6
Tetrahydrofuran	3.2	9.27	52.8	0.7	14.65	32.5
Acetonitrile	3.4	9.09	53.4	1.0	14.38	33.5
Dimethylsulfoxide	1.8	9.49	51.8	0.5	14.71	32.3
Dimethylformamide	2.5	9.40	52.2	0.6	14.32	33.7

^{a)} These polymerizations proceed heterogeneously.

III.5. Effect of zinc chloride on the copolymerization of AN with VS

It has been well known that the complexes of AN with LEWIS acids such as ZnCl₂, SnCl₄ and LiCl exhibit a different reactivity from the free

AN monomer²⁰). YABUMOTO *et al.*²¹) have reported that the addition of ZnCl_2 to the copolymerization of AN with styrene increases the alternating tendency as the result of complex formation with AN. Similarly, if ZnCl_2 is added to the AN/EVS copolymerization, the alternating tendency may increase. The results of copolymerization are shown in Fig. 14, from which it can be seen that alternating copolymer was obtained. This may be explained by the increased electron-accepting nature of AN as the result of complex formation with ZnCl_2 .

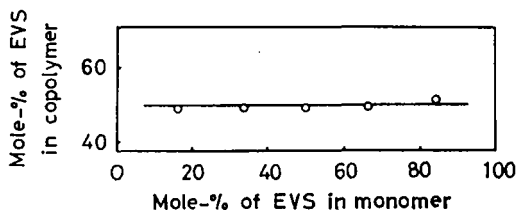


Fig. 14. Effect of zinc chloride on the copolymer condition in thermal copolymerization of EVS with AN in ethyl acetate at 60°C for 7 min: $([\text{EVS}] + [\text{AN}]) = 5.4$ mole/l., $[\text{ZnCl}_2]/[\text{AN}] = 0.5$. The results in the absence of ZnCl_2 , see Fig. 2

III.6. Thermal initiation and alternative copolymerizability

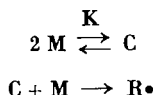
As described above, it was confirmed by spectroscopic measurements that there was a weak 1:1 donor-acceptor interaction between AN and VS, but its equilibrium constant was much smaller than that of MAN/EVS system (0.035 l/mole)⁴). This seems probably to be a contact-type charge transfer interaction based on a mesomeric polarization between both monomers. In the cases of MMA, EA and MA, however, it was impossible to observe spectroscopically such interaction with VS. Although spectroscopic measurements of the systems of DEF and DMM with VS were not made, these systems were not coloured, probably indicating that there are not strong interactions.

Since benzoquinone inhibited these thermal copolymerizations and since the resulting monomer reactivity ratios were in agreement with those by AIBN, it is clear that these copolymerizations proceed through a radical intermediate. Although the cationic polymerization of VS is induced with a very slow rate contrary to vinyl ether²¹⁻²⁵), any proof for cationic and anionic polymerizations was not obtained.

In general it is well known that the cross propagation and the cross termination are much favoured than the respective homopropagation and homotermiation in the radical copolymerization between donor and acceptor monomers²⁶). In these copolymerizations, the cross initiation may also be expected to occur readily. If the e values of acceptor monomers are used as a measure of their electron accepting nature, the ease

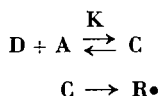
in cross propagation and cross initiation with electron donating VS monomer would increase as their e values increase positively. The result of Table 2 supports these considerations, to some extent.

The mechanism of thermal initiation of styrene polymerization has been investigated by many workers^{27,28)} and the following scheme proposed,



where C is an intermediate DIELS-ALDER adduct. This mechanism has been supported by the results of product analysis and kinetic study.

On the other hand, KOKUBO *et al.*²⁹⁾ have proposed the following mechanism for spontaneous alternating copolymerizations of *p*-dioxene and 1,2-dimethoxyethylene (D) with maleic anhydride (A),



where C is a charge transfer complex. This mechanism has been derived from kinetic results by assuming that the propagation proceeds *via* a reaction of only the complex monomer.

As described above, in the present copolymerization systems, the participation of the complexed monomer into propagation step is probably neglectable. The kinetic study of these thermal copolymerization was not made, but it may be assumed that the thermal initiation is induced by either radicals produced from the complex or the termolecular reaction of the complex with monomer.

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