

PHOTOCOPOLYMERIZATION OF MALEIC ANHYDRIDE AND VINYL ACETATE *

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ABSTRACT

The charge-transfer complex of maleic anhydride and vinyl acetate was copolymerized under UV light. The chain composition and structure of the copolymer were analyzed with conductometry and NMR, and the chain sequence was determined as alternating. The copolymerization rates at different feed ratios, temperatures and in different solvents were investigated, giving evidence to the very active involvement of the CT complexes in the copolymerization. Terpolymerization with acrylonitrile also showed that the complex mechanism was a proper one for this system.

INTRODUCTION

Reactions of the electron donor and acceptor systems where monomers make up one or both components frequently lead to polymerization either thermally or photochemically. Photocopolymerization of systems with comonomers as strong electron donor-accepter combinations has been the subject of many investigations^[1]. By comparison, however, less attention has been devoted to systems with weak donor-accepter combinations, especially to ones initiated photochemically. For studies on the kinetics and mechanism of such systems, maleic anhydride (MA) and vinyl acetate (VAc) being very popular monomers, constitute a convenient pair. There were some investigations on alternating copolymerization of MA with VAc using free radical initiator^[3,5], however, their photopolymerization was only reported by Aida et al.^[6]. In this paper we report the photo-initiated copolymerization of MA with VAc in various conditions. The mechanism of photoinitiation and chain propagation will also be discussed.

EXPERIMENTAL

Maleic anhydride was refined by distillation under reduced pressure. Vinyl acetate was purified as described in the literature^[2]. Acrylonitrile (AN) was dried with calcium chloride and again with calcium hydride before distillation. The fraction from 77 to 78 °C was collected. Other solvents used were treated with standard methods.

The copolymerization was carried out in a sealed tube. Before sealing the tube the reactant was bubbled with a stream of pure nitrogen for 10 minutes. Under the irradiation of UV light of wavelength 313 nm (specially made by prof. Xu of

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our institute for this purpose) the copolymerization was carried out in a thermostat at the required temperature. The product was precipitated with *n*-hexane and thoroughly washed with chloroform. In order to remove the unreacted MA completely, the precipitate was dissolved into acetone and reprecipitated again with *n*-hexane. Finally the product was dried under vacuum below 60 °C. Terpolymerization of MA, VAc and AN was carried out in the same way as copolymerization.

The copolymerization rates were measured using a dilatometer which was placed in a thermostat and kept at a fixed distance from the UV source.

The composition of copolymers was determined by conductometric titration^[3] with a BSD-A digital conductometer. The ¹³C-NMR spectra of the copolymers were taken on a Bruke AM 400 NMR spectrometer, from which the chain sequence was analyzed.

For measurements of UV spectra a Shimadzu UV-240 UV and visible spectrometer was used and for measurements at different temperatures a Beckman DU-7HS UV and visible spectrometer was used. The fluorescence measurements were performed on a SPEX Fluorology 212 fluorescence spectrometer.

The composition of terpolymers was evaluated by elemental analyses and conductometric titration. Elemental analyses were done by a Carlo-Erba 1106 automatic CHN-analyzer.

RESULTS AND DISCUSSION

The formation of MA and VAc charge-transfer (CT) complexes was confirmed by the UV and visible spectra. (Fig. 1) The spectrum of the mixture of MA and VAc displayed no new absorption peak and only a very small red-shift was observed. This implies that the system is a weak electron donor-acceptor combination. The equilibrium constant, *K*, between CT complex and the donor-acceptor pair was estimated via the Benesi-Hildebrand method^[4], i. e., calculated by measuring absorbance of solutions of different donor concentrations at a fixed wavelength which was 275 nm in the present study. At 25 °C and in chloroform, the measured equilibrium constant is 0.068 l/mol (*k*=0.06 l/mol reported by Claude Caze et al.^[3]) which is very small and is in accordance with the fact that the MA-VAc complex is weak CT complex.

Table 1 The assignment of chemical shifts in the ¹³C NMR spectrum of MA-VAc copolymer

	No.1 (ppm)	No.2 (ppm)	Literature value [5]
a	50.3	52.0	51.6 — 50.4
b	41.5	41.0	41.6 — 40.6
c	33.8	33.9	34
d	70.7	70.4	70.3 — 69.7
e	172.8	173.0	173.1
f	20.7	20.9	21
g	171.3	171.5	171.8
h	170.6	170.7	170.5

No.1: feed ratio of MA to VAc=20:80

No.2: feed ratio of MA to VAc=50:50

The chain composition and structure were analyzed by means of conductometric titration and NMR analysis. It was found that the MA and VAc copolymer polymerized photochemically in chloroform is an alternating copolymer regardless of their monomer feed molar ratios. Figure 2 is the monomer-copolymer composition diagram and Figure 3 is the ^{13}C -NMR spectrum of the MA-VAc copolymer. The assignment of chemical shifts was listed in Table 1 accompanied with data from literature.^[5] Aida et al.^[6] too reported that the copolymer synthesized via photocopolymerization of MA and VAc in dioxane was not an alternating copolymer, but with reactivity ratios of 0.10 and 0.005 for r_{MA} and r_{VAc} respectively. Data of their feed and copolymer compositions are given in Table 2 together with data from our experiments for comparison. Although the product of the two reactivity ratios calculated by Aida et al. is approximate to zero, their difference is as surprisingly big as 20 times. It can be seen from Table 2 that in Aida's experiments, the MA mole fractions of all copolymers obtained with different feed ratios are bigger than 0.5. This is probably owing to the effect of the solvent, dioxane, which is generally believed as an electron-donor. The effect of cyclic ether on the copolymerization of weak electron donor-accepter combinations will be further discussed in a separate paper.

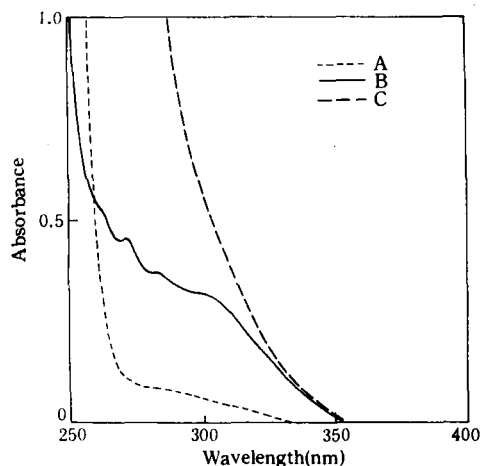


Fig.1 Absorption spectra of MA, VAc and their complex at 25 °C in chloroform
(A) VAc (5.4M), (B) MA (0.02M),
(C) VAc (5.4M) and MA (0.02M)

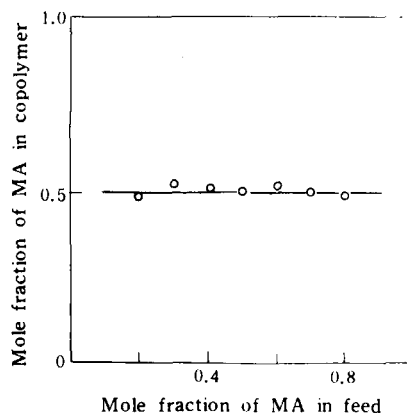


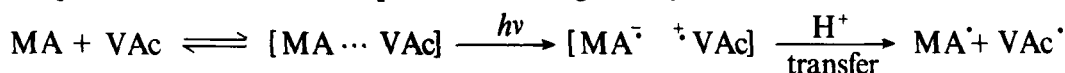
Fig.2 Free-copolymer composition curve for MA-VAc copolymer
[MA] + [VAc] = 2.0 M, Solvent: Chloroform, Temp.: 25 °C

Table 2 The composition of feed and copolymers

Feed (MA mol%)	80	70	60	50	40	30	20
Copolymer (MA mol%)	48.7	49.8	51.8	49.9	50.6	52.1	49.0
Copolymer (MA mol%)*	---	55.4	54.2	55.8	52.1	54.0	---

* Data from Aida et al.^[6]

For the photocopolymerization systems with CT complexes as comonomers, the photochemical initiation process can be generally written as follows:



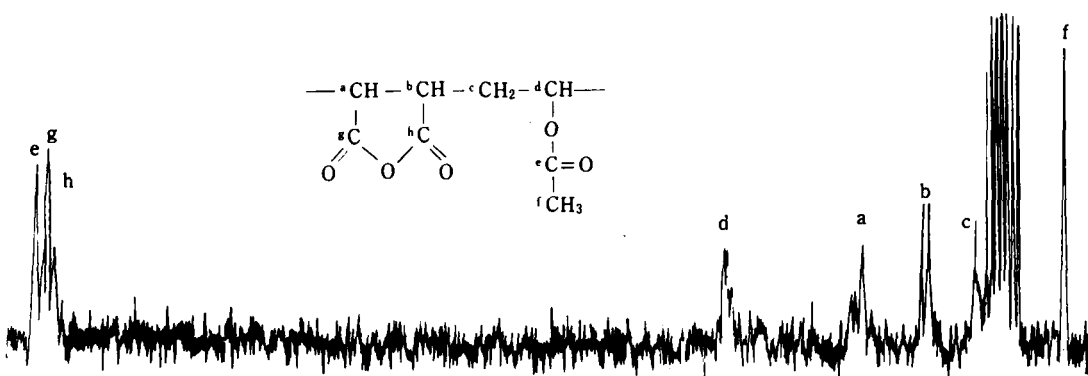


Fig. 3 ^{13}C -NMR spectrum of MA-VAc copolymer
Solvent: Hexadeuteroacetone, Internal standard: TMS

It is obvious that, if the total concentration of comonomers is constant, the polymerization rate should reach a maximum when the comonomer mole ratio is unity. In order to investigate the role of the CT complex in the present system, the copolymerization rates of systems with constant total molar concentrations but different molar ratios, i.e., different CT complex concentrations, were measured. The relation between polymerization rates and mole fractions of MA in feed represented in Figure 4, shows that the copolymerization rate in the feed range investigated, instead of having a maximum at the mole fraction of 0.5 as expected for systems with the highest CT complex concentration, rises with MA mole fraction until MA mole fraction approaches 0.7. The UV and visible spectrum of MA (Fig. 1) shows that at the wavelength of irradiation (313 nm) not only the CT complex of MA and VAc absorbs the light, but also MA does. Therefore, one may envisage that, under the irradiation, in addition to the CT complex of

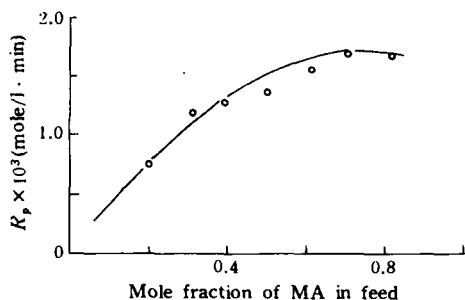


Fig. 4 Plot of R_p against the mole fraction of MA in chloroform $[\text{MA}] + [\text{VAc}] = 2.0 \text{ M}$, Temp.: 25°C , Solvent: Chloroform

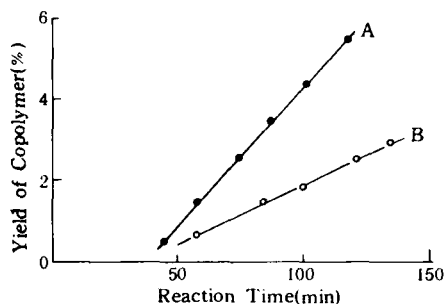


Fig. 5 Copolymerization rate of MA and VAc at 25°C in chloroform $[\text{MA}] + [\text{VAc}] = 2.0 \text{ M}$, $[\text{MA}] / [\text{VAc}] = 1$, (A): No additives; (B): With isoprene as the additive. $[\text{Isoprene}] = 0.01 \text{ M}$

MA and VAc, may have an $n-\pi^*$ transition and then form an exciplex with VAc to initiate the copolymerization in a way similar to the CT complex.

Solutions of MA and the MA/VAc mixture in chloroform and in cyclohexane

were subjected to measurements of the emission spectra, hoping to confirm the existence of such excited states. However, no fluorescence emission of either MA or MA-VAc complex was detected. This is probably due to the predominance of some other ways of dissipation of excitation energy, including the intersystem crossing which has life times of the order of 10^{-11} to 10^{-7} s, often fast enough to compete with fluorescence for deactivation. Indeed, for MA, Hammond had already reported the phosphorescence of MA with a triplet energy of $300 \text{ kJ/mol}^{[7]}$. It was found that in our system, the addition of a very small amount of isoprene (0.01 Mol/l) which is a very efficient triplet-quencher reduced the copolymerization rate considerably (Fig. 5), implying that a triplet process was involved. Although isoprene molecules may combine with growing chain and to retard the polymerization rate, it is conceivable that its effect is of less importance since its concentration is low. Thus it is most likely that under irradiation with UV light of 313 nm , MA can also be excited and contribute to the initiation, which explains the fact that the copolymerization rate increases with MA in the feed.

Since no matter what the monomer feed ratio is, the copolymer has an alternating chain structure, the ratio of the weight, W , of the copolymer produced to the volume shrinkage V of the reacting system is a constant and denoted as C . Therefore, a quite simple expression of the total copolymerization rate R_p can be derived as follows:

$$P_p = K dV / dt$$

$$K = C / [V(M_{MA} + M_{VAc})]$$

where V is the volume of the dilatometer. dV/dt is the rate of volume change due to polymerization which can be obtained experimentally. M_{MA} and M_{VAc} are molecular weights of MA and VAc, respectively. While keeping the monomer molar ratio of MA to VAc constant, by varying the total concentration of MA and VAc in chloroform, a series of polymerization rates at different concentrations were obtained, and thus from which the reaction order of 1.48 was deduced. (Fig. 6) This reaction order is similar to Barton's finding for the MA-styrene system^[1]. As described above, the product of the photopolymerization of MA and VAc has an alternating structure and consequently, the reaction can be regarded as an addition

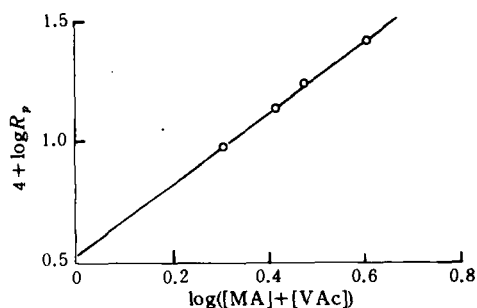


Fig. 6 Plot of $\log R_p$ against $\log ([MA] + [VAc])$
 $[MA]/[VAc] = 1$, Temp.: 25°C .
 Solvent: Chloroform

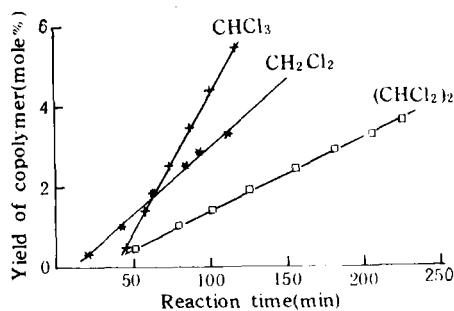


Fig. 7 Copolymerization rates of MA with VAc in various solvents
 $[MA] + [VAc] = 2.0 \text{ M}$, $[MA]/[VAc] = 1$, Temp.: 25°C

reaction of the CT complex. Therefore, an exponential value of 1.5 for the concentration of the CT complex should be expected. The discrepancy between the experimental and theoretical values for the total concentration of an equimolar MA-VAc mixture in chloroform is probably due to the fact that since the reaction rates were too small to be measured at low monomer concentrations and thus the reactions had to be carried out at relatively high concentrations which may in turn cause somewhat of the optical saturation, i.e., of the deviation from Lambert-Beer's law.

The kinetic behaviour of photocopolymerization of MA and VAc in different solvents and at different temperatures was studied. Their corresponding CT complex equilibrium constants for different temperatures were determined as well. The results are shown in Figures 7, 8 and Table 3. The dielectric constants of CHCl_3 , CH_2Cl_2 and $(\text{CH}_2\text{Cl})_2$ are 4.80, 9.08 and 10.36 respectively.

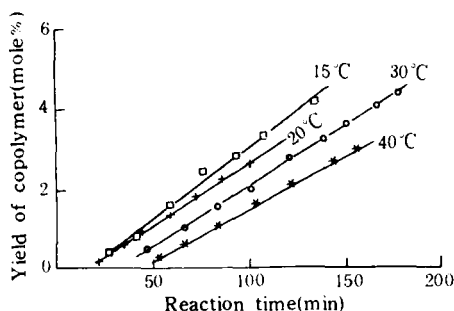


Fig. 8 Copolymerization rates of MA with VAc in chloroform at various temperatures. $([\text{MA}] + [\text{VAc}]) = 4.0 \text{ M}$, $[\text{MA}] / [\text{VAc}] = 1$

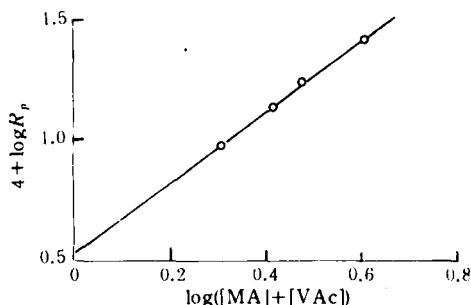


Fig. 9 Arrhenius plot of copolymerization of MA with VAc in chloroform $[\text{MA}] + [\text{VAc}] = 4.0 \text{ M}$, $[\text{MA}] / [\text{VAc}] = 1$

Table 3 The influence of temperature on K and R_p

Temp. ($^{\circ}\text{C}$)	$R_p \times 1000 \text{ (mol / l} \cdot \text{min)}$	$K \times 100 \text{ (l / mol)}$
15	1.43	7.09
20	1.27	6.80
30	1.19	6.41
40	1.06	5.95

$[\text{MA}] + [\text{VAc}] = 4.0 \text{ M}$, $[\text{MA}] / [\text{VAc}] = 1$

Solvent: chloroform

It can be seen from Fig. 7 that the copolymerization rate decreases with the increase of the solvents' polarity. For weak CT complex which is not sufficiently polar to initiate ionic polymerization, it is known that the increase of polarity causes the decrease of the CT complex equilibrium constant^[8] and thus the decrease of the copolymerization rate, which is in agreement with our results. Figure 8 clearly shows that the copolymerization rates increase reversely with temperature. It is conceivable that as the temperature is raised the CT complex becomes more unstable and hence the concentration of the CT complex drops and accordingly the copolymerization rate is reduced. Based on the data of copolymerization rates measured at different temperatures the apparent activation energy can be derived. Figure 9 is the Arrhenius plot of a system with a monomer feed molar ratio of

unity and a total concentration of 4.0 M. The calculated activation energy is approximate to zero (-1.98 kcal/mol). This strongly indicates the incorporation of the CT complex in the chain propagation process since the formation of the CT complex is an exothermic process and therefore the participation of the CT complex in the propagation reduces the apparent activation energy. In other words the higher the temperature, the smaller the CT complex equilibrium constant and the lower the copolymerization rate.

The mechanism of chain propagation was also investigated via the introduction of a third comonomer as reported by Iwatsuki et al.^[9]. The third comonomer used was acrylonitrile. Experiments on the terpolymerization with various feed composition were carried out and the degrees of conversion were kept below 5%. The compositions of the feed and products are listed in Table 4 and illustrated in Fig. 10. The results show that irrespective of the feed composition the mole ratio of MA to VAc in the terpolymer is a constant and equal to unity, indicating that

Table 4 Terpolymerization results for the system MA/VAc/AN

No.	Monomer feed			Terpolymer							
	[MA]	[VAc]	[AN]	Elemental analysis			MA-VAc part ^{a)}				Mole fraction MA-VAc
	mol·l ⁻¹	mol·l ⁻¹	mol·l ⁻¹	C	H	N	wt.-% of AN	wt.-% of C	wt.-% of H	mol-% of MA ^{b)}	
1	2.90	2.90	5.80	58.74	5.76	15.2	57.49	46.37	5.9	---	0.176
2	4.34	4.34	4.34	---	---	8.68 ^{c)}	32.86	---	---	---	0.370
3	4.90	4.90	2.94	53.65	5.04	4.87	18.42	51.27	4.63	48.7	0.561
4	5.42	5.42	2.10	52.19	5.00	2.83	10.71	50.30	4.92	---	0.706
5	5.60	5.60	1.21	52.06	4.68	1.27	4.79	50.43	4.90	50.8	0.851
6	2.40	7.28	2.90	51.13	4.57	5.58	21.12	46.63	4.27	---	0.518
7	1.61	8.08	2.92	55.30	4.90	6.73	25.48	50.98	4.64	---	0.457

a) Calculated composition of 1:1 MA and VAc part: C : H : O = 52.4 : 4.38 : 43.06.

b) Data from conductometric titration measurements.

c) Determined by the Kjeldahl method.

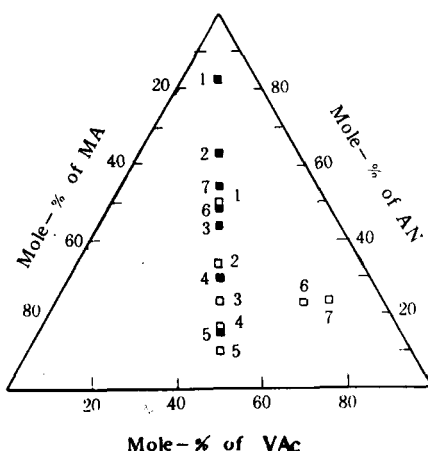


Fig.10 Terpolymerization of MA/VAc/AN.

(□) : Feed composition ; (■) : Terpolymer composition.

the CT complexes react as a unit with chain radicals. It was found that the experimental data can be well fitted to the copolymerization equation of Mayo-Lewis provided the terpolymerization is regarded as a copolymerization between the CT complex and AN. The reactivity ratios r_{CT} and r_{AN} were estimated according to Fineman-Ross's method^[10] and are 5.6 and 0.41 respectively, implying the high reactivity of the CT complexes. From these terpolymerizations it is evident that our results support Bartlett's propose^[11] on the mechanism of chain propagation in the alternating copolymerization with comonomers as CT complexes, i.e., the complex-mechanism, which suggests that CT complexes may act as a kind of monomer to react in chain propagation, and despite their usually low concentration in the system, it has a much higher reactivity, resulting in a copolymer with the main chain structure of repeated CT units.

CONCLUSION

By studying the UV spectra of MA, VAc and their mixture, the composition and chain sequence of MA and VAc copolymer, and the kinetic behaviour of the copolymerization of MA with VAc under UV light at various conditions, it was found that the MA and VAc copolymer has an alternating chain sequence, the copolymerization rate decreases with the increase of the solvents' polarity and the temperature due to the reduction of the concentration of the CT complex, showing the active involvement of the CT complex. In the reacting system, MA, in addition of being a component of the CT complex, can itself be excited by short wavelength UV light ($<313\text{ nm}$) and thus contributes to the initiation of the copolymerization. As to the role of the CT complex in the chain propagation, the terpolymerization of MA and VAc with AN indicates that the complex-mechanism is an appropriate mechanism for this system.

Keywords :

Maleic anhydride; Vinyl acetate; Charge-transfer complex; Photocopolymerization; Terpolymer

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