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## COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH PHENYLACETYLENE\*

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(Received 9 August 1975)

It was found by UV and NMR spectroscopy that maleic anhydride forms a charge transfer complex with phenylacetylene. Equilibrium constants of complex formation were determined at 30–50° and thermodynamic parameters of the complex calculated. A study was made of radical copolymerization of maleic anhydride with phenylacetylene and it was shown that the dependence of the rate copolymerization on the composition of the monomer mixture is determined by the tendency of monomer units to alternate and the breakage of growing chains on phenylacetylene. It was found that copolymers of maleic anhydride and phenylacetylene are paramagnetic.

RADICAL copolymerization of maleic anhydride (MA) with electron donor monomers has been studied very extensively. The interest in monomer systems of this type is mainly due to the fact that copolymers with alternating monomer units are formed in copolymerization. In most cases vinyl monomers are used as monomers—electron donors and copolymerization of MA with monomers of acetylene series is only reported in some papers [1, 2].

We examined radical copolymerization of MA with phenylacetylene (PA) in dioxane solution and molecular interaction between these monomers.

\* *Vysokomol. soyed.* **A17**: No. 10, 2333–2337, 1976.

MA was repeatedly recrystallized from dry chloroform and twice distilled *in vacuo*, m.p. 52.2°. PA was rectified in a laboratory column in argon, a fraction boiling at 141.5–142° taken,  $n_D^{20}$  1.5495. Dioxane was dried with Na metal and distilled over Na. Heptane was agitated with H<sub>2</sub>SO<sub>4</sub>, washed with KOH solution, water, dried with CaH<sub>2</sub> and Na and distilled. AID was recrystallized three times from ethyl alcohol and dried in vacuum.

Kinetics of copolymerization of MA with PA in dioxane solutions were examined in dilatometers with a capillary diameter of 0.08 cm. Monomer solutions containing an initiator (AID) were degassed by a conventional method with a residual pressure of 10<sup>-3</sup> torr. Degasified solutions were decanted into dilatometers filled with argon; copolymerization was carried out at 68°. Copolymers were precipitated with benzene and purified by two-fold reprecipitation with benzene from solutions in dioxane.  $\bar{M}_n$  was determined by the vapour phase method using a Hitachi Perkin-Elmer 115\* device. The composition of copolymers was determined by conductometric titration of copolymer solutions in 0.08 N dilute NaOH solution with a 0.1 N solution of hydrochloric acid. PMR spectra of MA and PA solutions in heptane were recorded using a "Jeol" INM-PS-100 radiospectrometer at 30, 40 and 50°. Hexamethyldisiloxane was used as standard. EPR spectra of copolymers were recorded using a PA-100 radio-spectrometer; IR spectra, using a UR-10 spectrometer. KBr pellets containing about 1 wt.% copolymer were used for recording IR spectra.

*Formation of intermolecular complexes between MA and PA.* A broad absorption band of low intensity with  $\lambda_{\max}=286$  nm was observed in the UV spectrum of the solution of a MA-PA mixture in heptane. This line is absent from spectra of each of the monomers. The type of band enables this line to be examined as a band of charge transfer of the MA-PA intermolecular complex. The low intensity of this band and overlapping with spectrum lines of individual components hinders the use of the UV spectroscopic method for obtaining quantitative results concerning complex formation of monomers. Therefore, to determine equilibrium constant  $K_c$  of complex formation, the PMR method was used. In PMR spectra of MA-PA solutions in heptane a shift is observed in the line, which corresponds to anhydride protons in the region of strong fields, compared with the position of this line in the spectrum of the MA solution in heptane (6.68 p.p.m.). When  $[PA] \gg [MA] K_c$  and  $[PA]$  are related by equation [3]

$$1/[PA] = \Delta_c K_c / \Delta_{\text{obs}} - K_c, \quad (1)$$

in which  $\Delta_{\text{obs}}$  is the difference of chemical shifts of anhydride protons in the anhydride spectrum and in the spectrum of the mixture with an electron donor,  $\Delta_c$  is the difference of chemical shifts of anhydride protons in the spectrum of anhydride and the spectrum of the "pure" complex.

From NMR results for solutions, in which  $[MA]$  was 0.06 mole/l. and  $[PA]$  varied between 2.7 and 7.25 mole/l, the value of  $K_c$  was determined at 30, 40 and 50°. Values of  $K_c$  obtained were used for calculating thermodynamic parameters of complex formation. Values of  $K_c$ ,  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  are tabulated.

For comparison the Table shows parameters of complex formation between MA and St, obtained by a similar method.

\* The authors are very grateful to A.G. Davtyan for measuring  $\bar{M}_n$  values of copolymers.

Judging by tabulated values the strength of the MA-PA complex, in spite of the conclusion made previously [2], is close to the strength of the MA-St complex. Considering this condition it was interesting to compare copolymerization of MA with PA and MA with St.

VALUES OF  $K_e$  AND THERMODYNAMIC PARAMETERS OF PROCESSES OF COMPLEX FORMATION BETWEEN MA AND PA

Complex	$T$ , °C	$K_e$ , l./mole	$-\Delta H$ , kcal/mole	$-\Delta S$ , e. un.	$\Delta G$ , kcal/mole
MA-PA	30	0.24			0.86
"	40	0.20	3.13	13.2	1.00
"	50	0.17			1.13
MA-St	30	0.336	1.5	7.4	—

\* St—styrene; results of an earlier study [4].

*Copolymerization of MA ( $M_1$ ) with PA ( $M_2$ ).* Figure 1 shows the relation between copolymer composition and the composition of the monomer mixture. Using the Finemann-Ross method copolymerization constants were determined from these results for a MA-PA monomer pair. Constants calculated by the method of least squares are  $0.065 \pm 0.005$  and  $0.076 \pm 0.006$ , respectively. Thus, the

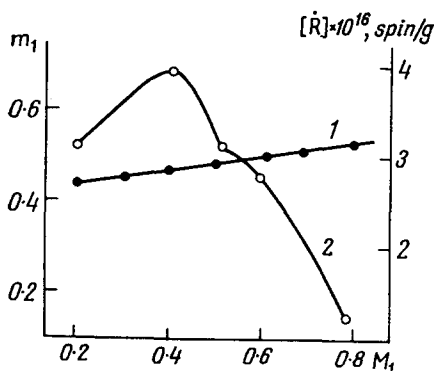


FIG. 1

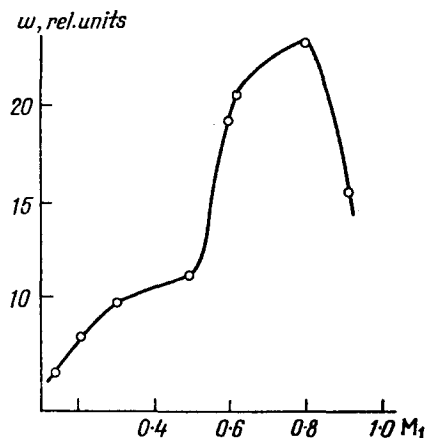


FIG. 2

Fig. 1. Relation between copolymer composition (1), the concentration of paramagnetic particles  $R$  (2) and the composition of the monomer mixture.

Fig. 2. Relation between the overall rate of copolymerization and the composition of the monomer mixture.

tendency of monomer units to alternate in copolymerization of MA with PA is quite obvious, although not so markedly as in copolymerization of MA with St. It should be noted that constants of copolymerization obtained differ consider-

ably from the values given previously [2] where, for the case of radiation copolymerization of these monomers by a radical mechanism it was found that  $r_1=0.05$  and  $r_2=0.5$ .

The kinetic order of polymerization for the initiator is 0.83 and independent of the composition of the monomer mixture. Chain rupture evidently takes place chiefly by a mono-molecular mechanism. It may be assumed that rupture on PA is the main reaction, as observed in homopolymerization of PA by the action of benzyl peroxide [5].

MW of the copolymer varies little and without any regularity according to the composition if the monomer mixture  $\bar{M}_n$  is in the range of 2800–3700. It is interesting that  $\bar{M}_n$  is practically independent of the concentration of the initiator:  $\bar{M}_n$  of copolymers obtained with a 1 : 1 monomer ratio and initiator concentrations of 10 and 0.5 wt.%, are 3600 and 3900, respectively

The fact that the degree of polymerization  $\bar{P}_n$  is independent of initiator concentration and the composition of the monomer mixture may be explained as follows: as a consequence of a marked tendency of monomer units to alternate and assuming that chain rupture occurs as a result of the reaction of a growing radical with PA, we have

$$k_{12} [\dot{\text{M}}\text{A}] [\text{PA}] = k_{21} [\dot{\text{P}}\text{A}] [\text{MA}] \quad (2)$$

$$\bar{P}_n = \frac{2k_{12} [\dot{\text{M}}\text{A}] [\text{PA}]}{k'_r [\text{MA}] [\text{PA}] + k''_r [\text{PA}] [\dot{\text{P}}\text{A}]}, \quad (3)$$

where  $k_{12}$ ,  $k_{21}$ ,  $k'_r$  and  $k''_r$  are constants of chain extension and rupture. Excluding radical radiation concentrations from equation (3) using equation (2) we obtain a formula for  $\bar{P}_n$  free from terms dependent on initiator concentration

$$\bar{P}_n = \frac{2k_{12}}{k'_r + \frac{k''_r k_{12}}{k_{21}} ([\text{PA}]/[\text{MA}])} \quad (4)$$

Assuming that  $k'_r > k''_r k_{12}/k_{21}$ ,  $\bar{P}_n$  is independent of  $[\text{PA}]/[\text{MA}]$  or this relation is negligible.

Figure 2 shows the dependence of the overall rate of copolymerization on the composition of the monomer mixture. The relation is external. This relation is determined by two factors: 1) alternation of monomers added to the growing radical; 2) rupture of growing chains of PA.

It is known that curves showing the relation between the rate of copolymerization and the composition of the monomer mixture in copolymer formation with alternating monomer units have a maximum. In most cases mixture compositions close to the equi-molecular correspond to the maximum, but sometimes the maximum is displaced to higher concentrations of one of the monomers. Thus, it is reported [6] that in copolymerization of MA with St in THF the maximum is displaced to higher concentrations of MA and it is assumed that

the displacement is due to the interaction of MA with the solvent. It may be assumed that in copolymerization of MA with PA the displacement of the maximum to the range of ratios  $[MA]/[PA] \approx 4$  is due to a reduction in the rate of rupture with a reduction in the content of PA in the monomer mixture.

*Study of copolymers of MA-PA by spectroscopic methods.* The IR spectrum of the MA-PA copolymer contains absorption bands typical of the anhydride ring: 1785 and 1860  $\text{cm}^{-1}$  (bond stretching vibrations of the C=O bond); 1215  $\text{cm}^{-1}$  (bond stretching vibrations of the C—O bond). In the range of 1450–1500  $\text{cm}^{-1}$  there are two absorption bands due to skeletal vibrations of the benzene ring and in the range of 700, 760 and 785  $\text{cm}^{-1}$  absorption bands are observed which are due to out-of-plane deformation vibrations of C—H bonds of the benzene ring. Low-intensity bands in the region of 1580 and 1630  $\text{cm}^{-1}$  are evidently due to absorption of the benzene ring conjugated with the double bond and bond stretching vibrations of the C=C bond.

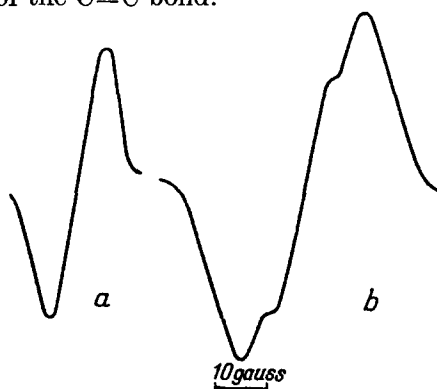
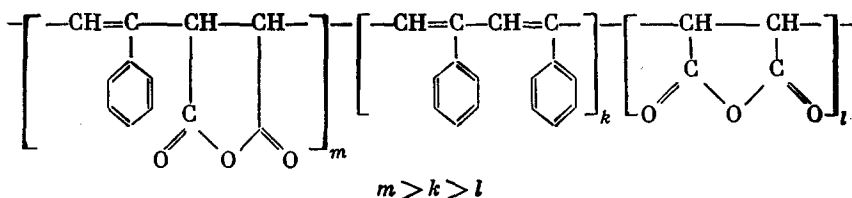


Fig. 3. EPR spectra of MA-PA copolymer samples obtained by photopolymerization (a) and in the presence of AID (b).

MA-PA copolymers are paramagnetic; the type of EPR spectra depends on the method of obtaining copolymers. The spectrum of the copolymer obtained by photopolymerization by the action of light with a wave length  $> 310$  nm is a singlet with  $\Delta H_{pp}$  9.90 gauss (Fig. 3a) similar to the singlet of polyphenylacetylene ( $\Delta H_{pp}$  9.87 gauss). This indicates the presence in the copolymer chain of blocks consisting of several PA units and confirms the assumption concerning the presence of these units in the MA-PA copolymer previously made on the basis of results of a thermochemical study [7]. The spectrum shown in Fig. 3b corresponds to the copolymer obtained in the presence of AID. This spectrum contains a singlet with the same value for  $\Delta H_{pp}$  as the signal of the copolymer obtained in photo-polymerization and another signal with  $\Delta H_{pp}$  23.3 gauss. This signal should, apparently be ascribed to the radical formed during the rupture by the initiator radical of a hydrogen atom from the main chain of the copolymer. Rupture of hydrogen from the anhydride unit to form a radical conjugated with a double bond of the PA unit appears to be the most likely.

The overall concentration of paramagnetic particles in copolymer samples depends on copolymer composition (Fig. 1). The extremal dependence is probably due to the fact that the concentration of radicals corresponding to a singlet with  $\Delta H_{pp}$  of 9.90 gauss is determined by the content of fragments consisting of several PA units and the concentration of radicals giving a signal with  $\Delta H_{pp}$  of 23.3 gauss depends on fraction of MA-(PA) $_n$  fragments in the copolymer ( $n \geq 1$ ).

Judging by IR and EPR spectroscopic results and constants of copolymerization, the MA-PA copolymer has the following structure :



Translated by E. SEMERE

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## EFFECT OF DIAMINE STRUCTURE ON THE BEHAVIOUR OF SOLIDIFIED EPOXY-AMINE SYSTEMS\*

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(Received 27 February 1976)

The effect of the structure of a diaminoalkane molecule on the degree of conversion was studied by IR spectroscopy in solidification of epoxide oligomers with and without solvents. The dependence of glass temperature, deformation strength, adhesion and protective diffusion properties of coatings on the length of the hydrocarbon chain in the diaminoalkane molecule was examined.

\* *Vysokomol. soyed.* **A18**: No. 10, 2338-2342, 1976.