

9. B. WUNDERLICH and G. BAUER, Heat Capacity of Linear Polymers (Transl. from English and German by Yu. K. Godovskii), p. 238, Mir, M., 1972
10. Yu. K. GODOVSKII, Thermophysics Methods for Polymer Study, p. 216, Khimiya, M., 1976
11. G. V. VINOGRADOV, Yu. G. YANOVSKII, V. N. KULEZNEV and T. A. IVANENKO, Kolloid. zh. **28**: 640, 1966

Polymer Science U.S.S.R. Vol. 28, No. 5, pp. 1215-1221, 1986
Printed in Poland

0032-3950/86 \$10.00+.00
© Pergamon Journals Ltd.

COMPLEX-RADICAL COPOLYMERIZATION OF DICYCLOPENTADIENE WITH MALEIC ANHYDRIDE*

Z. I. RZAYEVA, L. V. MEDYAKOVA and U. KH. AGAYEV

Institute of Chloroorganic Syntheses, Azerb. S.S.R. Academy of Sciences

(Received 3 September 1984)

Radical copolymerization of dicyclopentadiene with maleic anhydride has been investigated. The reaction proceeds through a stage where intermediate products—intermolecular donor-acceptor complexes—are formed that are highly reactive and substantially influence the copolymerization. The reactivity ratios have been determined for free monomers as well as for monomers bonded in the complex: $r_{12} = 0.096 \pm 0.01$, $r_{21} = 0.061 \pm 0.01$, and $r_{2C} = 0.0024 \pm 0.001$, $r_{2C_1} = 0.032 \pm 0.005$, $r_{2C_2} = 0.0026 \pm 0.001$. A quantitative kinetic analysis shows that reactions that involve the complexed monomers prevail in the elementary propagation steps and a "complex" mechanism of chain growth has been proposed for alternating copolymerization of dicyclopentadiene with maleic anhydride.

CYCLOOLEFINS belong to the less reactive monomers with π - p conjugation and, in comparison to their acyclic analogs, are difficult to copolymerize by the radical mechanism; nevertheless, they react relatively easily with maleic anhydride (MA).

Dicyclopentadiene (DCPD), tricyclo-5,2,1,0,10,6-decadiene-3,8, and also some other cycloolefins are known to copolymerize by the radical mechanism with MA, forming alternating copolymers [1-5]. It is the aim of this study to elucidate the mechanism governing radical copolymerization of DCPD with MA and to characterize quantitatively the participation of intermolecular complexes in the elementary steps of chain propagation.

DCPD prepared by dimerization of cyclopentadiene was used as a mixture of endo- and exo-isomeric forms (b.p. $88^\circ\text{C}/7.327\text{ kPa}$, $n_D^{25} 1.5110$, $d_4^{25} 0.9870$).

MA was purified by recrystallization from benzene and sublimed *in vacuo*; m.p. 52.8°C .

* Vysokomol. soyed. **A28**: No. 5, 1089-1094, 1986.

Kinetics of copolymerization was followed dilatometrically in the region of small conversions ($<10\%$); the dilatometer volume was 13.0 ml, the capillary diameter was 2.5 mm. The results were evaluated taking into account the coefficient of contraction.

IR spectra were measured with the instrument UR 20 between 450 and 600 cm^{-1} (KBr cell) and between 2600 and 3200 cm^{-1} (LiF cell).

^1H NMR spectra were registered with the spectrometer Tesla BS 487B at 80 MHz; methyl ethyl ketone was the solvent and hexamethyldisiloxane served as the internal standard.

The copolymerization was carried out in dioxane either in the dilatometer or in a glass ampoule at 60–90°C under nitrogen in the presence of benzoyl peroxide (1%). The copolymer was isolated by precipitation in diethyl ether, washed several times with petroleum ether, and vacuum-dried at 40°C to constant weight. The maximum yield of the alternating copolymer was 68.5%, m.p. 235–265°C, $[\eta]=0.042$ dl/g (dioxane, 25°C), unsaturation 10.9%, oxygen number 476 mg KOH/g. The product was a white powder, easily soluble in acetone and in other polar solvents.

The copolymer composition was determined by potentiometric titration (Potentiometer LPM-220), elemental analysis, and IR spectrometry.

Results of experiments with DCPD/MA copolymerization are collected in Table 1 and show the composition of the product to be mostly close to 1 : 1. However, with increasing relative amount of MA in the reaction mixture its content in the copolymer approaches 58 mole%, apparently because of some branching due to the double bond in the diene comonomer. The yield, intrinsic viscosity, and copolymerization rate all attain their highest values at the equimolar ratio of the two monomers.

The opposite character of polarity of double bonds in the two comonomers (DCPD and MA) brings about a possibility of intermolecular donor-acceptor interaction leading to the formation of an equilibrium charge-transfer complex (CTC). ^1H NMR spectra show an upfield chemical shift of the symmetric protons in MA in its mixtures with DCPD when the latter monomer is in excess, $[\text{DCPD}] \geq [\text{MA}]$ (see Table 2).

Protons in π -bonds of the cyclopentene and norbornene fragments give rise to a complex multiplet in the NMR spectrum, where the most intensive peak at 5.025 ppm is shifted downfield to 5.05 ppm at the composition corresponding to $[\text{DCPD}] : [\text{MA}] = 10 : 1$.

These data confirm that a charge transfer complex is indeed formed; the equilibrium constant $K_e=0.06$ l./mole has been determined according to the Ketelaar

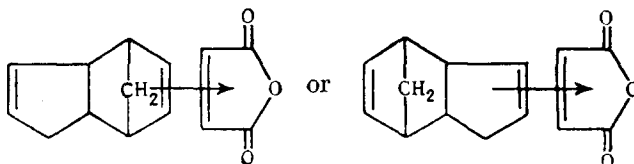
TABLE 1. RADICAL COPOLYMERIZATION OF DCPD (M_1) WITH MA (M_2)
Solvent dioxane, initiator benzoyl peroxide (1%); $[\text{dioxane}] : ([M_1] + [M_2]) = 1$; 15 hr at 70°C

| Composition of monomer mixture, mole % | | Yield, % | Oxygen number, mg KOH/g* | Elemental analysis, %* | | Copolymer composition, mole % | | $[\eta]$, dl/g dioxane | $v \times 10^3$, %/sec |
|--|---------|----------|--------------------------|------------------------|------|-------------------------------|---------|-------------------------|-------------------------|
| $[M_1]$ | $[M_2]$ | | | C | H | $[m_1]$ | $[m_2]$ | | |
| 70 | 30 | 34.6 | 410 | 77.28 | 5.37 | 50.66 | 42.34 | 0.028 | 0.78 |
| 60 | 40 | 49.7 | 480 | 76.80 | 5.50 | 50.05 | 49.95 | 0.031 | 0.96 |
| 50 | 50 | 68.5 | 487 | 72.10 | 6.22 | 49.84 | 50.16 | 0.042 | 1.83 |
| 40 | 60 | 41.3 | 510 | 67.00 | 6.83 | 47.22 | 52.78 | 0.032 | 1.12 |
| 30 | 70 | 26.5 | 560 | 59.00 | 7.36 | 41.84 | 58.16 | 0.019 | 0.88 |

* Calculated for alternating copolymer: C 73%, O 2%, H 6.08%; oxygen number 486 mg KOH/g.

equation by plotting (cf. Fig. 1) $1/\Delta$ against $1/[\text{DCPD}]$ (since DCPD is the electron donor). The plot in Fig. 1 is linear, indicating that the complex has the equimolar (1 : 1) composition.

It is obvious that the two possible complexes



must be formed with different probabilities, but the obtained results are insufficient to resolve this problem.

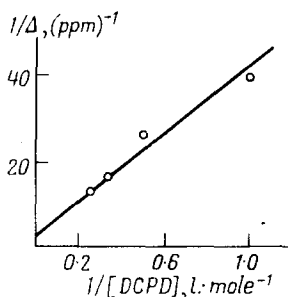


FIG. 1. The quantity $1/\Delta$ as a function of reciprocal DCPD concentration;¹ determination of equilibrium constant K_e of the formation of complex between DCPD and MA ($1/\Delta_k$ is the intercept of the straight line and the slope is $1/\Delta_k \cdot K_e$). Measured in MEK at 37°C, $[\text{DCPD}] \gg [\text{MA}]$.

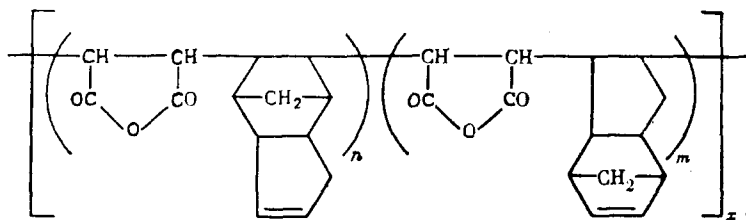
It has been established [1, 2] that the strongly screened double bond in the bicycloheptane structure shows the highest reactivity in radical copolymerization with MA. The properties of the double bond in the five-membered ring can be judged on the basis of IR spectra of DCPD itself and of the copolymer (see Fig. 2).

The following bands are characteristic for the spectrum of DCPD (cm^{-1}): 1635 ($\nu_{\text{C}=\text{C}}$ of the bicyclopentane group), 1605 ($\nu_{\text{C}=\text{C}}$ of the cyclopentane group), 915, 940, 990 (the five-membered ring), and intensive bands between 700 and 800 (δ_{CH} of the six-membered ring).

New bands at 1720, 1770, and 1840 cm^{-1} ($\nu_{\text{C}=\text{O}}$), 1250 cm^{-1} ($\delta_{\text{C}-\text{O}-\text{C}}$) appear in the spectrum of the copolymer, while the band at 1605 cm^{-1} disappears and marked changes are observed in the region 900–1000 cm^{-1} ; the band at 1450 cm^{-1} (δ_{CH_2} of the five-membered ring and also those at 760 and 785 cm^{-1} (δ_{CH} of the six-membered ring) are preserved.

These observations lead us to maintain that the double bond in the cyclopentene ring participates to a certain extent in the copolymerization of DCPD with MA, and this reaction is facilitated under more severe conditions (at high temperatures and in the presence of excess MA).

The following general structure of the alternating copolymer DCPD/MA emerges from the results of elemental analysis, NMR and IR spectroscopy:



where $n \gg m$.

The monomer reactivity ratios (r_1 and r_2) were determined from the modified Jaacks equation [7] where the monomer concentrations before and after copolymerization were replaced by the corresponding values of optical density D ,

$$r_1 = \left(\log \frac{D_1^t}{D_1^0} \right) / \left(\log \frac{D_2^t}{D_2^0} \right) \quad \text{and} \quad r_2 = \left(\log \frac{D_2^t}{D_2^0} \right) / \left(\log \frac{D_1^t}{D_1^0} \right)$$

D_1^t and D_2^t are the respective optical densities of analytical absorption bands of the two monomers at time t , D_1^0 and D_2^0 those at time $t=0$.

As neither monomer homopolymerizes under these conditions, the reaction could be followed up to high conversions to determine the monomer reactivity ratios with sufficient accuracy. Calibration curves I^{485}/I^{620} (or I^{565}/I^{620}) \rightarrow $[M]$ were constructed prior to quantitative data evaluation; I^{485} and I^{565} are the band intensities (baseline corrected) of deformation vibrations of double bonds in DCPD and MA, respectively, I^{620} is the intensity of dioxane absorption band that showed the least variation, taken as reference; $[M]$, the monomer concentration, was expressed in mole %.

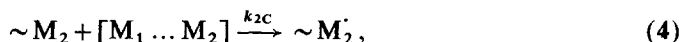
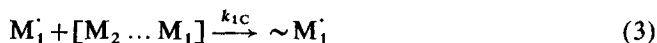
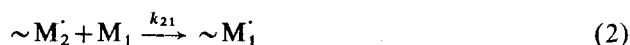
The monomer reactivity ratios calculated from the data in Table 3 are $r_1 = 0.096 \pm 0.01$, $r_2 = 0.061 \pm 0.01$; the corresponding constants for DCPD in the $Q-e$ diagram are $Q_1 = 0.023$, $e_1 = -0.017$.

The reactivity ratios characterizing the reaction of the intermolecular complexes DCPD...MA and MA...DCPD with the MA' radical will be designated r_{2C} , r_{2C1} , r_{2C2} ; they have been evaluated from the data in Table 1 by means of the Seiner-Litt equation [8], i.e., by plotting $(y-1)$ against $(1/[M_1]) - (y-1)/r_2[M_2]$ (where $y = [m_2]/[m_1]$); the slope of the plot defines r_{2C}/K_e and the intercept yields r_{2C}/r_{2C2} . The resulting values, $r_{2C} = 0.0024 \pm 0.004$, $r_{2C2} = 0.032 \pm 0.005$, $r_{2C1} = 0.0026 \pm 0.001$, prove the charge transfer complexes to be very reactive with respect to MA'; the highest activity shows the complex DCPD...MA.

The results of kinetic measurements enabled us to characterize the dependence of the copolymerization rate on a number of factors: temperature, overall monomer concentration, initiator concentration, the ratio of monomers in the reaction mixture.

The reaction order with respect to the monomers was found to be $m = 1.17$, with respect to the initiator it was $n = 0.50$. The apparent activation energy of DCPD/MA copolymerization, obtained by plotting the rate constant against the reciprocal absolute temperature, was $E_a = 87$ kJ/mole.

Since neither DCPD nor MA can homopolymerize under the given conditions, the elementary steps of chain propagation, involving the free or the complexed monomers, can be written as



where M_1 represents DCPD, M_2 stands for MA, $[M_1 \dots M_2]$ and $[M_2 \dots M_1]$ designate the charge transfer complexes; k_{12} , k_{21} , k_{1C} , k_{2C} are the rate constants characterizing the addition of free monomers or of CTC's onto the growing radical.

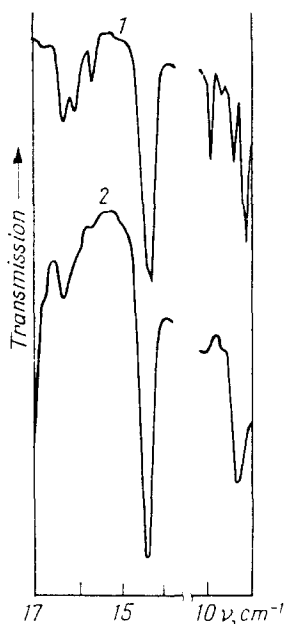


FIG. 2

FIG. 2. IR spectra of DCPD (1) and of the copolymer DCPD/MA (2).

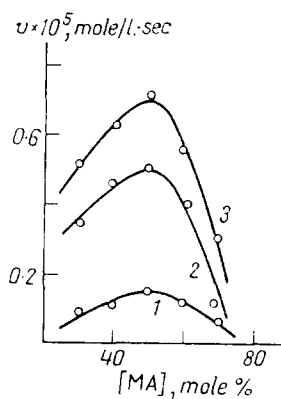


FIG. 3

FIG. 3. Rate of copolymerization of DCPD with MA plotted against the composition of the monomer mixture; overall monomer concentration $[M] = 1.5$ (1), 2.8 (2), and 3.6 mole/l. (3).

Kinetic equations valid for alternating copolymerization [9] enabled us to distinguish the most prevalent reactions in the above scheme.

Figure 3 shows the dependence of the copolymerization rate on the composition of the reaction mixture for different overall monomer concentrations; all curves go through a maximum and its position remains the same for concentrations varying between 1.5 and 3.6 mole/l. This is possible if either reactions (1) and (2) ("free monomer mechanism") or reactions (3) and (4) ("complex mechanism") are operative.

TABLE 2. CHARACTERISTICS OF PMR SPECTRA OF DCPD-MA MIXTURES (MEK at 37°C, [DCPD] \gg [MA])

| [MA], mole/l. | [DCPD], mole/l. | δ^{MA} , ppm | | $\Delta = \delta_{\text{free}}^{\text{MA}} - \delta_{\text{obs}}^{\text{MA}}$, ppm |
|---------------|-----------------|----------------------------|------------|---|
| | | free | in mixture | |
| 0.1 | 1.0 | 7.250 | 7.225 | 0.025 |
| 0.1 | 2.0 | 7.250 | 7.212 | 0.038 |
| 0.1 | 3.0 | 7.250 | 7.187 | 0.063 |
| 0.1 | 4.0 | 7.250 | 7.170 | 0.080 |

TABLE 3. CHARACTERISTICS OF IR SPECTRA OF DCPD (M_1) AND MA (M_2) PRIOR TO AND AFTER COPOLYMERIZATION, USED FOR DETERMINING THE MONOMER REACTIVITY RATIOS r_1 AND r_2

| Initial mixture, mole/l. | | Reaction mixture at time t , mole/l. | | 565 cm^{-1} (δ_{CH} in -CH=CH-MA) | 485 cm^{-1} (δ_{CH} in -CH=CH-DCPD) |
|--------------------------|-----------|--|-----------|---|---|
| $[M_1]_0$ | $[M_2]_0$ | $[M_1]_t$ | $[M_2]_t$ | D | D |
| 4.28 | 0.48 | — | — | 0.8561 | 0.1614 |
| — | — | 4.188 | 0.163 | 0.8388 | 0.0550 |
| 0.39 | 3.63 | — | — | 0.1134 | 0.6180 |
| — | — | 0.0695 | 3.515 | 0.0203 | 0.5966 |

TABLE 4. DETERMINATION OF THE QUANTITIES k_{1c}/k_{12} AND k_{2c}/k_{21}

| $F = [M_1]/[M_2]$ | $a \times 10^5$ | $b \times 10^5$ | $f = a/b$ | $2f/K_e$ | $F = [M_1]/[M_2]$ | $a \times 10^5$ | $b \times 10^5$ | $f = a/b$ | $2f/K_e$ |
|-------------------|-----------------|-----------------|-----------|----------|-------------------|-----------------|-----------------|-----------|----------|
| 0.538 | 0.08 | 0.025 | 3.2 | 106.6 | 1.500 | 0.34 | 0.025 | 13.6 | 453.3 |
| 0.666 | 0.14 | 0.025 | 5.6 | 186.6 | 2.333 | 0.46 | 0.025 | 18.4 | 613.3 |
| 1.000 | 0.23 | 0.025 | 9.2 | 306.6 | | | | | |

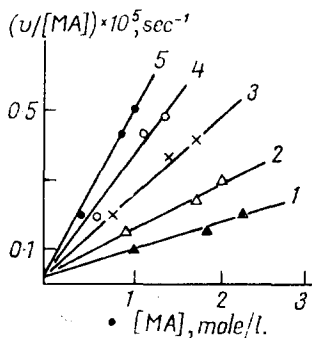


FIG. 4

FIG. 4. The ratio $v/[MA]$ as a function of $[MA]$; determination of the slope, a , and the intercept, b , for different compositions of the monomer mixture: $F = [\text{DCPD}]/[\text{MA}] = 0.538$ (1), 0.666 (2), 1.0 (3), 1.5 (4), and 2.333 (5).

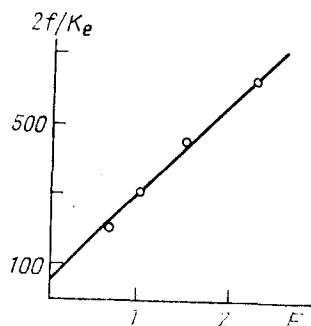


FIG. 5

FIG. 5. The quantity $2f/K_e$ plotted against F ; determination of the contribution of CTC to chain propagation (the slope is k_{1c}/k_{12} , the intercept defines k_{2c}/k_{21}).

To resolve the problem, the equation for the rate of copolymerization was rewritten in terms of the equilibrium constant K_e of complex formation,

$$\frac{v}{[M_2]} = \frac{v_{in}^\dagger K_e (k_{21} k_{1C} F^2 + k_{12} k_{2C} F)}{k_0^\dagger (k_{12} + k_{21} F)} [M_2] + \frac{v_{in}^\dagger 2 k_{12} k_{21} F}{k_0^\dagger (k_{12} + k_{21} F)} \quad (5)$$

where $F = [M_1]/[M_2] = [\text{DCPD}]/[\text{MA}]$; equation (5) can be written in a simplified form as $v/[M_2] = a[M_2] + b$, where the meaning of a and b is obvious.

Plotting $v/[M_2]$ against $[M_2]$ (see Fig. 4) for different values of F , one can find the slope a and the intercept b ; putting $a/b = f$, we then have

$$2f/K_e = k_{1C}/k_{12} F + k_{2C}/k_{21} \quad (6)$$

The values of a , b , f , $2f/K_e$ obtained for different values of the monomer ratio F are collected in Table 4.

The data are plotted according to equation (6) in Fig. 5 and yield $k_{1C}/k_{12} = 300$ (from the slope) and $k_{2C}/k_{21} = 50$ (from the intercept).

These values represent the ratio of rate constants characterizing the addition of CTC and of the free monomer onto the same end radical of the growing chain and are so high that one may indeed speak of the "complex" mechanism of alternating copolymerization between DCPD and MA.

Translated by M. KUBÍN

REFERENCES

1. N. G. GAYLORD and A. B. DESHPANDE, *Polymer Preprints* **18**: 522, 1977; *J. Macromol. Sci.* **A11**: 1795, 1977
2. M. RÄTZSCH, M. ARNOLD and R. HOYER, *Plaste und Kautschuk* **24**: 731, 1977
3. Z. I. KHALILOVA, Z. M. RZAYEV and U. Kh. AGAYEV, *Azerb. Khim. Zh.*, **2**, 73, 1975
4. Z. M. RZAYEV, S. I. SADYKH-ZADE and L. V. BRYKSINA, *Vysokomol. soyed.* **B16**: 8, 1974 (Not translated in *Polymer Sci. U.S.S.R.*)
5. S. CESCA, A. ROOGERO and N. RASSARINI, *Chimie et industrie* **55**: 403, 1973
6. J. A. A. KETELAAR, C. STOLPE, A. GOUDSMIT and W. DZCUBAS, *Rec. trav. chim.* **71**: 1104, 1952
7. V. V. JAACKS, *Makromol. Chem.* **161**: 161, 1972
8. J. A. SEINER and M. LITT, *Macromolecules* **4**: 308, 1971
9. G. S. GEORGIEV and V. P. ZUBOV, *Eur. Polym. J.* **14**: 93, 1978