

INVESTIGATIONS IN THE FIELD OF RADIATION-INDUCED SOLID-STATE POLYMERIZATION

PART XVII. THE POLYMERIZATION OF 5-CARBOXY-BICYCLO-(2.2.1)-HEPTENE-(2)
AND ITS COPOLYMERIZATION WITH MALEIC ANHYDRIDE*

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The monomers which had hitherto been studied from the point of view of their radiation-induced polymerization in the solid state can be classified into three groups, according to their chemical structures: 1. vinyl monomers, 2. saturated cyclic monomers and 3. compounds polymerizing by way of the opening of the C=O or C≡N bonds.

Acenaphthylene is the only unsaturated cyclic compound whose radiation-induced polymerization in the solid state has so far been studied [1]. It was found that polymerization in the solid phase proceeds more rapidly in the presence of air than without it; polymerization rate is proportional to the first power of the dose rate and polymerization kinetics in the solid state has a linear character. With increasing temperature polymerization rate increases monotonously and above the melting point polymerization proceeds in the liquid phase at a considerably higher rate than in the solid phase. The radiation-induced copolymerization of acenaphthylene with maleic anhydride was also studied [2]. This system forms an eutectic and at the temperature of the experiment (probably above the melting point of the eutectic mixture) either polyacenaphthylene or the 1 : 1 copolymer of the two components was formed.

The study of the laws governing the radiation-induced polymerization in the solid phase of unsaturated cyclic compounds promised some interesting results. Therefore we undertook to subject to investigation the radiation-induced polymerization and copolymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) (norbornene carboxylic acid) both in the liquid and in the solid phase. The study of the benzoyl peroxide initiated polymerization of the compound in the liquid phase and its copolymerization with maleic anhydride was already the subject of other papers [3, 4].

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Experimental

The synthesis of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) was described in an earlier communication [3]. The 41.5°C melting point corresponds to the exo-form [5]. The compound forms monoclinic crystals with the following main characteristics: $a = 10.97 \text{ \AA}$, $b = 11.4 \text{ \AA}$, $c = 12.3 \text{ \AA}$, $\beta = 100^\circ$, $Z = 8$, D calculated = $1.21 \text{ g} \cdot \text{ml}^{-1}$, D measured = $1.21 \text{ g} \cdot \text{ml}^{-1}$, probable steric group $P \ 21/a$; work on a more detailed clarification of the crystal structure is in progress [6].

Maleic anhydride of analytical grade manufactured by Reanal was used. Polymerization was studied in glass ampoules by excluding oxygen [7]. Polymerization kinetics in the liquid phase was followed dilatometrically, in the solid phase gravimetrically. The polymers were separated from an acetone solution by precipitation with benzene, the copolymers from the acetone solution by precipitation with ether. The phase transformation temperature of the monomer was determined by differential thermal analysis [7], the structures of the polymers and copolymers were studied on the basis of their infrared spectra which were obtained with a UR 10 Zeiss Jena spectrometer using the KBr pellet technique, or in paraffin oil suspension. The composition of the copolymers was determined by potentiometric titration by the method described earlier [4].

Experimental results and discussion

Figure 1 shows the kinetic curves obtained for the gamma-radiation induced liquid phase polymerization of norbornene carboxylic acid for different temperatures and dose rates. In the liquid phase polymerization kinetics has a linear character, the rate increases proportionally to the first power of the dose rate and the brutto activation energy can be determined from the temperature dependence of the polymerization rates ($E_p - \frac{1}{2}E_t = 2.52 \text{ kcal per mole}$). Radiation-induced polymerization in the liquid phase is inhibited by benzoquinone, diphenyl-picryl hydrazide, i.e. by the inhibitors of radical mechanisms, confirming the radical character of polymerization. Chain termination is in all probability not bimolecular. The relatively low value of the brutto activation energy indicates a higher activation energy of the chain termination processes.

The kinetic curves of the radiation-induced solid-phase polymerization of norbornene carboxylic acid are shown in Fig. 2 for different temperatures and dose rates. The kinetic character of solid-phase polymerization is linear, polymerization rate changes proportionally to the first power of the dose rate.

Figure 3 shows the changes in polymerization rate vs the temperature in the different phases. In the liquid phase polymerization rate decreases with decreasing temperature, in the solid phase polymerization rate passes through a maximum and this maximum is characteristically not in the vicinity of the melting point, but about 10°C lower than the latter, around 30°C . To clarify the causes of this phenomenon, the possible transformation of the solid monomer was studied by differential thermal analysis. The results are

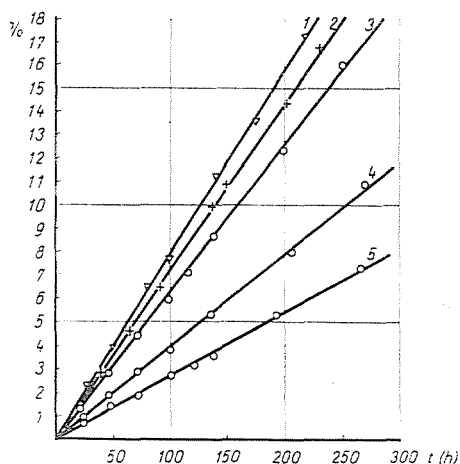


Fig. 1. The kinetic curves of the radiation-induced polymerization of 5-carboxy-bicyclo-(2.2.1)-heptene-(2) in the liquid phase 1. 65°C , dose rate 1.05×10^5 r/h, 2. 55°C , dose rate 1.05×10^5 r/h, 3. 46.5°C , dose rate 1.05×10^5 r/h, 4. 46.5°C , dose rate 0.72×10^5 r/h, 5. 46.5°C , dose rate 0.49×10^5 r/h

shown in Fig. 4. A heat effect indicating phase transformation appears quite clearly around 30°C in the solid monomer. The nature of this phase transformation is still subject to an investigation, but it may be stated, on the basis of our present knowledge, that we are dealing here with a phenomenon similar to that observed in the case of e.g. acrylonitrile [8, 9], namely that due to phase transformation a rearrangement of the molecules takes place in the solid phase. In other words, it may be assumed that there is a considerable increase in the mobility of the molecules creating favourable conditions for the increase of the polymer chain in the solid phase.

The post-polymerization of norbornene carboxylic acid was studied after preliminary irradiation at -78°C and post-polymerization in the solid phase at 20° , 30° and 35°C . Under these conditions no polymers were formed. The fact that post-polymerization had no effect may be explained by the phase transformation around 30°C , as it seems quite probable that the active centres formed by preliminary irradiation recombine at the temperature at which the molecules have a higher mobility, and before being able to initiate a polymerization process.

The effect of benzoquinone and diphenyl-picryl hydrazile on the solid-phase polymerization of norbornene carboxylic acid was studied at 30°C with inhibitor concentrations between 0.5 and 2 weight per cent. The rate of solid-phase polymerization of the system containing 2 weight per cent

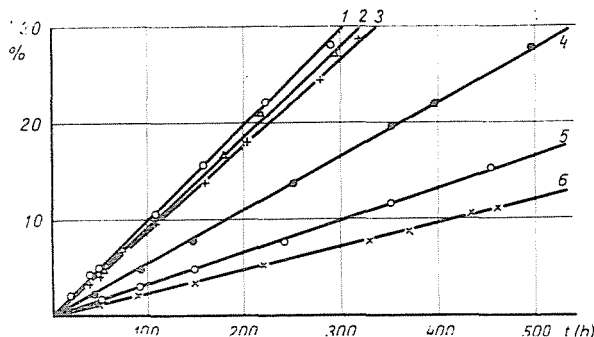


Fig. 2. The kinetic curves of the radiation-induced polymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) in the solid phase: 1. 30°C, dose rate 1.05×10^5 r/h, 2. 20°C, dose rate 1.05×10^5 r/h, 3. 39°C, dose rate 1.05×10^5 r/h, 4. 0°C, dose rate 1.05×10^5 r/h, 5. 0°C, dose rate 0.72×10^5 r/h, 6. 0°C, dose rate 0.49×10^5 r/h

inhibiting agent was about one third of the polymerization rate of the system without inhibitor, and polymerization rate decreased linearly with increasing inhibitor concentration.

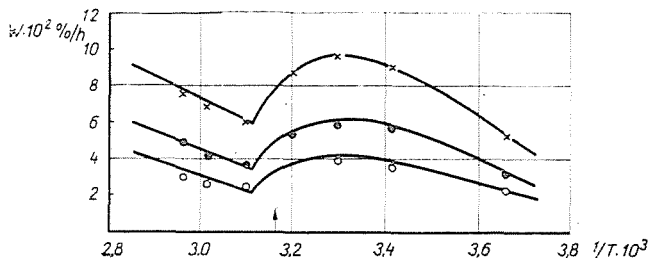


Fig. 3. The rate of the radiation-induced polymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) vs the temperature. Irradiated with 1.05×10^5 r/h

The infrared spectra of the polymers formed in the liquid and solid phases are shown in Fig. 5. The absorption band at 2960 cm^{-1} is characteristic of the cyclopentane ring, the bands at 1425 and 715 cm^{-1} of double bonds with hydrogens in the cis-position.

Thus, structures of the polymers formed by the irradiation of norbornene carboxylic acid can be presented in the following way:

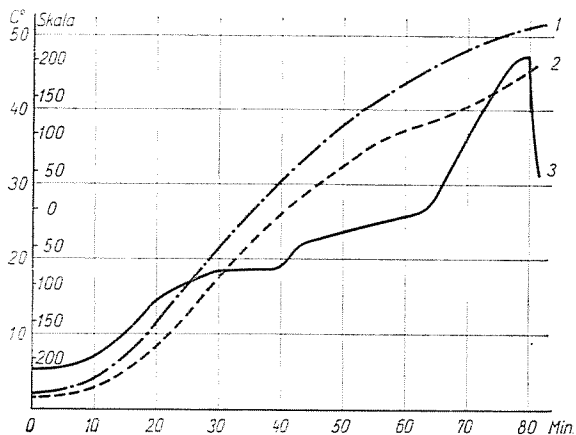
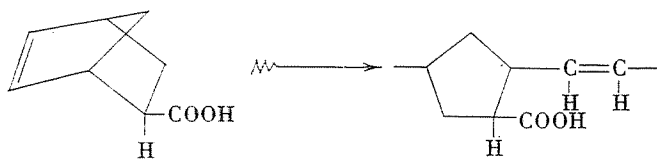


Fig. 4. Differential heat effect during heating of solid 5-carboxy-bicyclo-(2.2.1)-heptene-(2) indicating a phase transformation

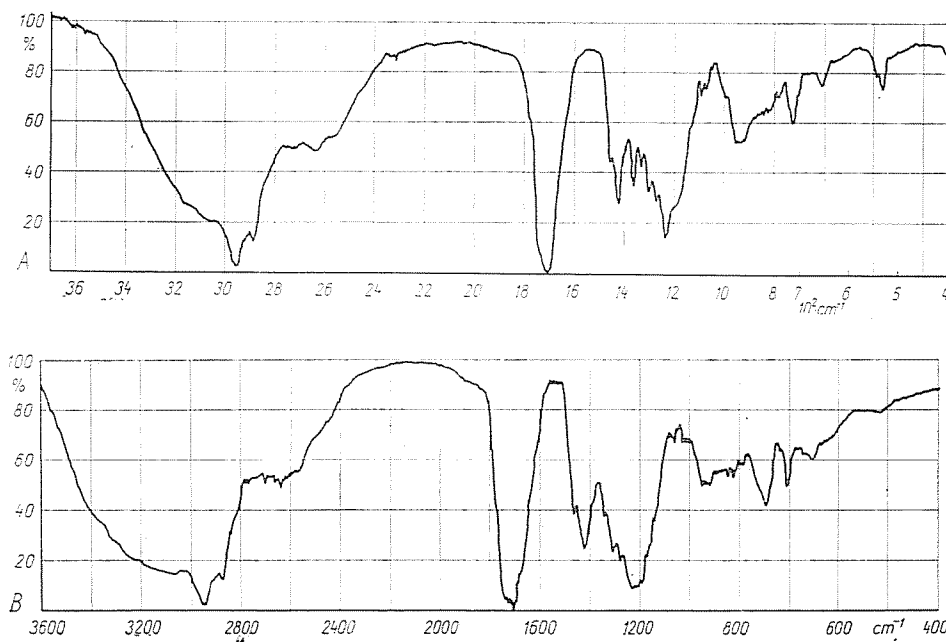


Fig. 5. The infrared spectra of the polymers of 5-carboxy-bicyclo-(2.2.1)-heptene-(2) formed in the liquid (A) and in the solid (B) phase

The radiation-induced copolymerization of norbornene carboxylic acid with maleic anhydride was studied in both the solid and the liquid phase. Figure 6 shows the kinetic curves of the copolymerization of monomer mixtures with varying compositions at 65°C when irradiated with a dose rate of 1.05×10^5 r/h. The kinetic curves of the copolymerization process reveal a linear character. Fig. 7 shows the copolymerization rate vs the composition of the initial monomer mixture; a maximum appears at 0.5 mole fractions.

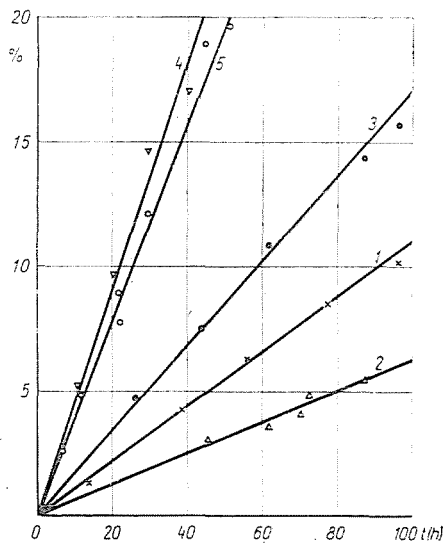


Fig. 6. The kinetic curves of the copolymerization of 5-carboxy-bicyclo-(2.2.1)-heptene-(2) (M_2) and maleic anhydride (M_1) in the liquid phase at 65°C, irradiated with 1.05×10^5 r/h. Ratio of the components: 1. 1.95 mole% M_1 and 98.0 mole% M_2 ; 2. 3.9 mole% M_1 and 96.1 mole% M_2 ; 3. 9.8 mole% M_1 and 90.2 mole% M_2 ; 4. 35 mole% M_1 and 65 mole% M_2 ; 5. 69.5 mole% M_1 and 30.5 mole% M_2 .

Changes in the composition of the copolymer formed by liquid-phase copolymerization vs the initial monomer composition are shown in Fig. 8. The character of this curve is different from the copolymerization curve for benzoyl peroxide initiated liquid-phase copolymerization [4]. In radiation-induced copolymerization, though maleic anhydride is still the more reactive monomer, a convex curve is obtained, while in benzoyl peroxide initiated copolymerization an inflection point appears at 0.5–0.6 mole fraction maleic anhydride content. The value of the copolymerization constant of the radiation-induced liquid-phase copolymerization calculated by the method of FINEMAN and ROSS is for maleic anhydride $r_1 = 12.35$ and for norbornene carboxylic acid $r_2 = 0.03$. For liquid-phase copolymerization in the presence of benzoyl peroxide initiator the same constants are: $r_1 = 0.36$ and $r_2 = 0.08$. This difference of two orders in the values of r_1 may perhaps be explained by changes

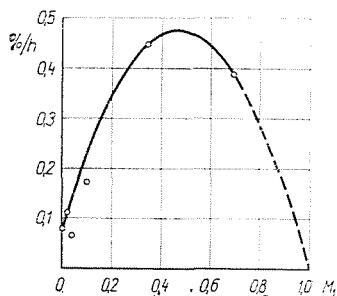


Fig. 7. Rate of the radiation-induced copolymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) with maleic anhydride in the liquid phase vs the composition of the initial monomer mixture

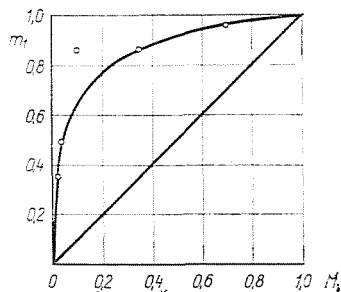


Fig. 8. The composition of the copolymers formed in the radiation-induced copolymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) in the liquid phase vs the composition of the initial monomer mixture

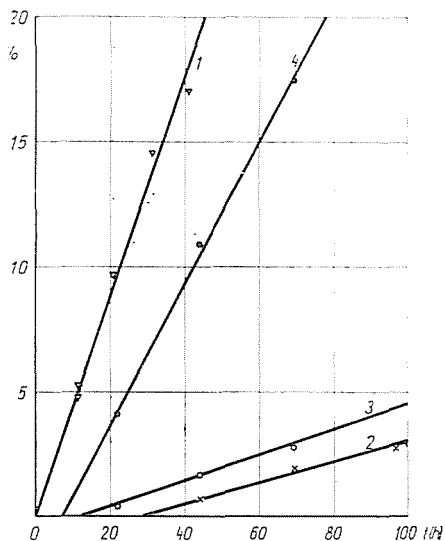


Fig. 9. The kinetic curves of the radiation-induced copolymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) (M_2) and maleic anhydride (M_1) in the liquid phase in the presence of benzoquinone at 65°C, irradiated with 1.05×10^5 r/h: 1. 35 mole% M_1 and 65 mole% M_2 , 2. the same as 1 + 1 w% benzoquinone, 3. the same as 1 + 0.5 w% benzoquinone, 4. the same as 1 + 0.1 w% benzoquinone

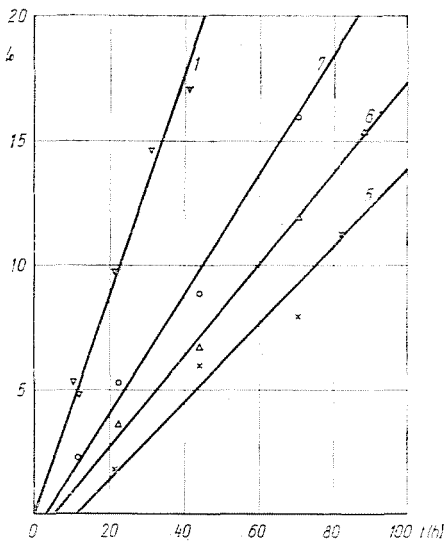


Fig. 10. The kinetic curves of the radiation-induced copolymerization of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) (M_2) and maleic anhydride (M_1) in the liquid phase at 65°C in the presence of diphenyl-picryl hydrazile, irradiated with 1.05×10^5 r/h: 5. the same as 1 (Fig. 9) + 1 w% diphenyl-picryl hydrazile, 6. the same as 1 (Fig. 9) + 0.5 w% diphenyl-picryl hydrazile, 7. the same as 1 (Fig. 9) + 0.1 w% diphenyl-picryl hydrazile

in the mechanism of the process, but as may be seen from Figs 9 and 10 benzoquinone and diphenyl-picryl hydrazile cause a well-defined inhibition period in the radiation-induced liquid phase copolymerization. It seems to be more promising to seek for the explanation of the phenomenon in the dead-end

polymerization. As stated in an earlier communication [3], the benzoyl peroxide initiated polymerization of norbornene carboxylic acid proceeds according to the dead-end mechanism. It is known from JOSHI's work [10] that the homopolymerization of maleic anhydride in the presence of large quantities of benzoyl peroxide proceeds in the liquid phase also according to the dead-end mechanism. Thus, if two monomers homopolymerizing according to dead-end kinetics are copolymerized in the presence of benzoyl peroxide, their behaviour

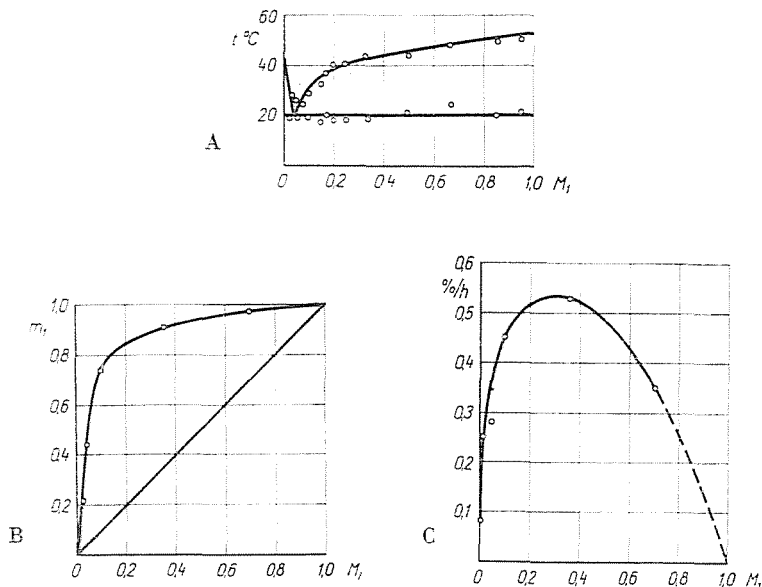


Fig. 11. The 5-carboxy-bicyclo-(2:2:1)-heptene-(2) + maleic anhydride system. A: phase diagram, B: the composition of the copolymer formed in the solid phase vs the composition of the initial monomer mixture, C: rate of solid phase copolymerization vs the composition of the initial monomer mixture at 10 $^{\circ}\text{C}$ irradiated with 1.05×10^5 r/h

will be different from that in radiation-induced liquid-phase copolymerization, for in the latter case the system receives continuously new initiation by irradiation. This difference has a significant effect on the copolymerization process and on the composition of the copolymer formed, thus also on the values of r_1 and r_2 .

The phase diagram of norbornene carboxylic acid and maleic anhydride is shown in Fig. 11/A. An eutectic with a melting point at 19 $^{\circ}\text{C}$ is formed at 4 mole per cent maleic anhydride content. Fig. 12 shows the kinetic curves for various initial monomer compositions when radiation-induced copolymerization is carried out at 10 $^{\circ}\text{C}$ with 1.05×10^5 r/h dose rate. The curve in Fig. 11/B represents the composition of the copolymer formed in the solid phase vs the composition of the initial monomer mixture and that in Fig. 11/C the copoly-

merization rate calculated from the conversion values after 50 hours reaction as a function of the composition of the initial monomer composition. The results show a marked discrepancy from the copolymerization behaviour in the solid phase of the earlier investigated two-component systems [11, 12, 13]. In the norbornene carboxylic acid—maleic anhydride system the maximum of the copolymerization rate lies not at the eutectic composition (4 mole per cent of maleic anhydride), but at 30 mole per cent maleic anhydride content. Neither is the composition of the copolymer identical with that of the eutectic,

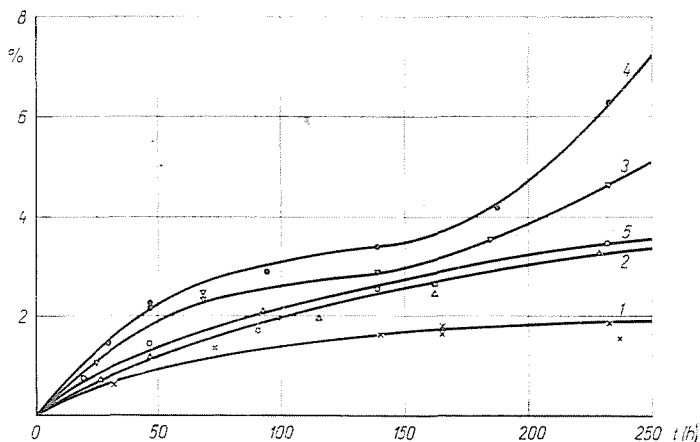


Fig. 12. The kinetic curves of the radiation-induced copolymerization of mixtures of 5-carboxy-bicyclo-(2,2,1)-heptene-(2) (M_1) and maleic anhydride (M_2) in the solid phase at 10°C , irradiated with 1.05×10^5 r/h: 1. 1.9 mole% M_1 and 98.1 mole% M_2 , 2. 3.9 mole% M_1 and 96.1 mole% M_2 , 3. 9.8 mole% M_1 and 90.2 mole% M_2 , 4. 34.9 mole% M_1 and 65.1 mole% M_2 , 5. 69.5 mole% M_1 and 30.5 mole% M_2 .

but depends on the composition of the initial monomer mixture. The radiation-induced copolymerization process in the solid phase can be described by the values of the copolymerization constants (determined by the FINEMAN—ROSS method) which are $r_1 = 17.3$ and $r_2 = 0.07$. These values are of the same order as those obtained for radiation-induced copolymerization in the liquid phase, and also differ from the constants of copolymerization initiated by benzoyl peroxide in the liquid phase ($r_1 = 0.36$ and $r_2 = 0.08$). As has already been shown the polymerization of norbornene carboxylic acid proceeds in the solid phase according to linear kinetics. Maleic anhydride does not polymerize in the solid phase, obviously because the distance of the double bonds, which would be involved in the polymerization process, is so great [14, 15] that it cannot be overcome by the thermal mobility of the molecules in the solid phase. We have demonstrated in our earlier work [16] that in the eutectic the mobility of monomer molecules may increase to a degree that a monomer pair, whose components are alone incapable of polymerization in the solid phase, may form

a copolymer at the eutectic composition and at other compositions, too, along the heterogeneously contacting crystal surfaces. In the present case the polymerization of one of the components proceeds in the solid phase according to linear kinetics, while the other does not polymerize in the solid phase. It seems that on the addition of the component which alone does not polymerize in the solid phase (maleic anhydride), favourable conditions from the point of view of copolymerization are formed on the crystal interfaces. These favourable conditions improve up to the eutectic composition and beyond it, as the mobility of the maleic anhydride molecules increases at the interface

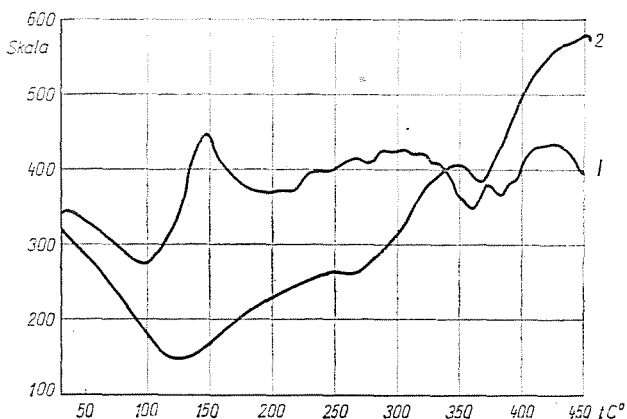


Fig. 13. The derivatogram of poly-[5-carboxy-bicyclo-(2,2,1)-heptene-(2)](curve 1) and of the copolymer formed in the solid phase from an initial monomer mixture containing 12 mole% of maleic anhydride (curve 2)

of the copolymer in the eutectic system and of the maleic anhydride crystals resulting in a considerably higher self-addition of maleic anhydride. The accelerating effect of the polymer on the polymerization of monomers which react in the solid phase according to accelerated kinetics has been proved experimentally [17]. These findings are supported by the fact that in an initial monomer mixture with 20 mole% maleic anhydride content a copolymer containing more than 80 mole% of maleic anhydride is formed. Comparison of Figs 11/B and 11/C also shows quite clearly that up to about 30 mole% of maleic anhydride content copolymerization rate increases beyond the eutectic composition along the heterogeneous interface of the copolymer and the maleic anhydride component. Further increase of the maleic anhydride content results in a reduction of copolymerization rate as higher maleic anhydride concentrations reduce the possibility of heterogeneous interfaces.

The copolymer nature of the polymer product was proved partly by choosing for precipitation from the acetone solution a solvent (ether) in which both

homopolymers are soluble, and partly by derivatographic tests. Figure 13 shows the derivatogram of the poly-(norbornene carboxylic acid) homopolymer (curve 1) and the derivatogram of a product obtained by the copolymerization in the solid phase of a mixture containing 12 mole% of maleic anhydride (curve 2). There is a marked difference between the two curves. In Fig. 14

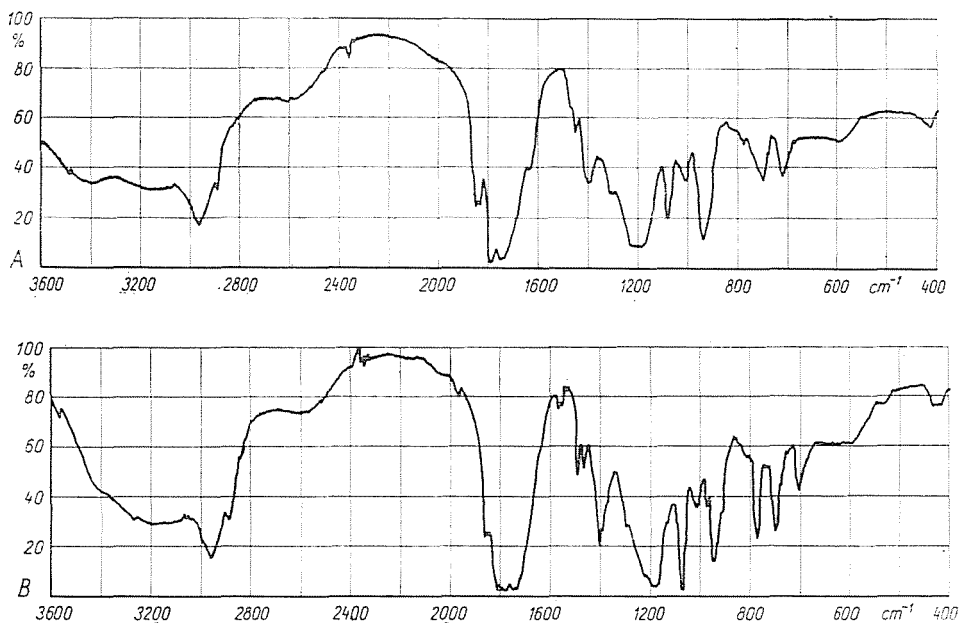


Fig. 14. The infrared spectra of 5-carboxy-bicyclo-(2.2.1)-heptene-(2) (A) and of the copolymer obtained in the solid phase (B)

the infrared spectra of copolymers obtained in the liquid and in the solid phase are shown. The absorption band at 2960 cm^{-1} indicates the presence of a cyclopentane ring, the bands at 1425 and 715 cm^{-1} that of double bonds with hydrogens in the *cis*-position, while the band at 1240 cm^{-1} proves the presence of incorporated maleic anhydride units. Thus, the formation of a copolymer was proved by three independent methods.

Summary

The radiation-induced liquid- and solid-phase polymerization of 5-carboxy-bicyclo-(2;2;1)-heptene-(2) and its copolymerization with maleic anhydride was studied. The structure of the copolymer was investigated by three methods. Both polymerization and copolymerization have a linear kinetic character. The solid-phase polymerization of norbornene carboxylic acid shows a maximum 10°C below the melting point indicating a second-order transition temperature. The two-component solid system forms an eutectic with a corresponding change in copolymerization rate; the composition of the copolymer points to a significant self-addition of maleic anhydride.

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