INVESTIGATION OF SOLID PHASE POLYMERIZATION. XL

THE ROLE OF CRYSTALLOGRAPHIC FACTORS IN THE SOLID PHASE POLYMERIZATION OF N-VINYLPHTHALIMIDE

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There is a close relationship between the crystal structure of the system to be polymerized and the laws governing solid phase polymerization of monomers [1].

The effect of the crystal structure on the course of polymerization is manifest by the primary and secondary crystal-chemical characteristics. As primary characteristic, the lattice structure of a given monomer is considered, that is, the geometry and size of the elemental cell, and the mutual arrangement and orientation of monomer molecules inside the elemental cell. The concept of secondary crystal-chemical characteristic includes crystal texture, crystallite size and the nature and amount of lattice defects.

The role of the primary characteristics can be clarified in the case of the so-called polymorphous monomers, as here different lattice structures are associated with the same chemical structure. Investigations on the solid phase polymerization of the polymorphs of acrylonitrile [2, 3], tributylvinylphosphonium bromide [4], methacrylic acid [5] have revealed that the features of polymerization are considerably influenced by primary crystal-chemical characteristics.

We prepared two enantiotropic and one monotropic modifications of N-vinylphthalimide (NVPI) and studied their direct and postpolymerization in the solid phase [6, 7]. It has been established that the polymerization ability of the various modifications is different. Using radical inhibitors and chemical initiators it has been proved that the solid phase polymerization induced by γ-irradiation follows a free radical mechanism.

In this paper the role of the primary and secondary crystal-chemical characteristics is further investigated. The secondary characteristics were modified by changing the conditions of crystallization and by adding foreign substances to the monomers.

Experimental

N-vinylphthalimide was prepared according to Ref. [8], and recrystallized three times from isopropyl alcohol. Succinimide used as additive was also triply recrystallized from isopropyl alcohol (m.p.: 125 °C). N-ethylphthalimide

was prepared by reacting phthalic anhydride with 50% aqueous ethylamine. During refluxing the solution formed after mixing the two components N-ethyl-phthalimide separated as an oily phase, which crystallized upon cooling down. It was also recrystallized three times from isopropyl alcohol (m.p.: 76 °C). Thermal behaviour of the various modifications of NVPI was studied by optical polarization methods [9], while the phase relations of the two-component system by X-ray analysis [10] and thermoanalytical methods.

The various modifications of the NVPI were prepared as reported earlier [7].

Results and discussion

N-vinylphthalimide is known to have two enantiotropic (I and II) and one monotropic (III) modifications [7]. I (m.p.: 86 °C) is stable in the temperature range of 40.5–86 °C, while II (m.p.: 75 °C) below 40.5 °C. Modification III is unstable below its melting point (82 °C). As a consequence of the kinetic control of the solid phase transitions, the different modifications can be stored in the unstable state and — as has been shown earlier [7] — their solid phase polymerization is comparable under identical experimental conditions. According to our experience, modification I transforms into modification II within a storage time of 3—8 days at room temperature.

The secondary crystal-chemical characteristics can be modified either by changing the conditions of the crystallization or by additives. Increasing the cooling rate (non-isothermal crystallization) or the extent of supercooling (isothermal crystallization) results in the decrease of the crystallite size and the increase of the amount of crystal defects. Additives that form eutectic mixtures with the monomer lead to the formation of crystal mixtures of very fine texture. Upon increasing the amount of additive (up to the eutectic composition) increasing fractions of the monomer assume eutectic structure; at the eutectic composition and at higher concentrations of the additive the total amount of the monomer is present as the eutectical crystal mixture [10].

With the change of the secondary crystal-chemical characteristics the storability of the modifications in an unstable state also change. In some cases it was not possible to store the substance in an unstable state, in others (e.g. with additives) the storability in this state improved.

Samples with various particle size and texture of modifications I and II of NVPI were prepared in order to investigate the effect of secondary crystal-chemical characteristics. (Modification III is unsuitable for this purpose because of its instability.) The solid phase polymerization of the samples prepared in such a way was studied at 30 °C, with an irradiation dose rate of 1.67×10^5 rad/h.

With NVPI I kinetic curves for polymerization were recorded for two particle sizes (ca. $3.5 \times 10^2 \times 3.5 \times 10^2$ and $28 \times 10^2 \times 4 \times 10^2$ μm) crystallized
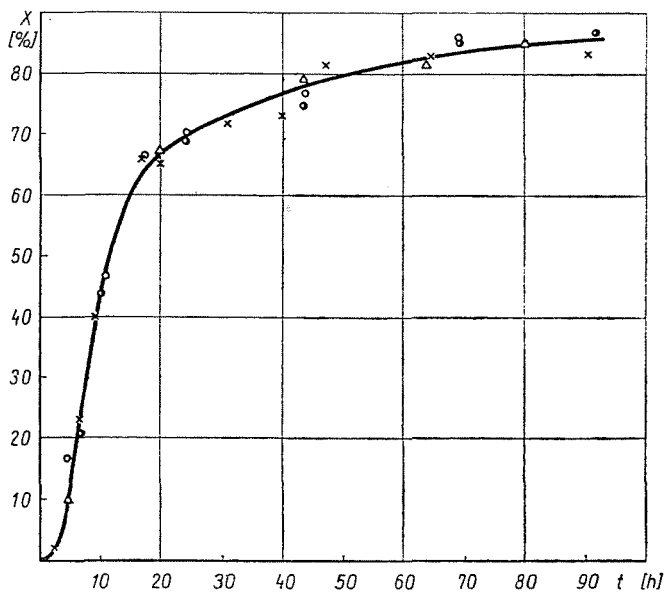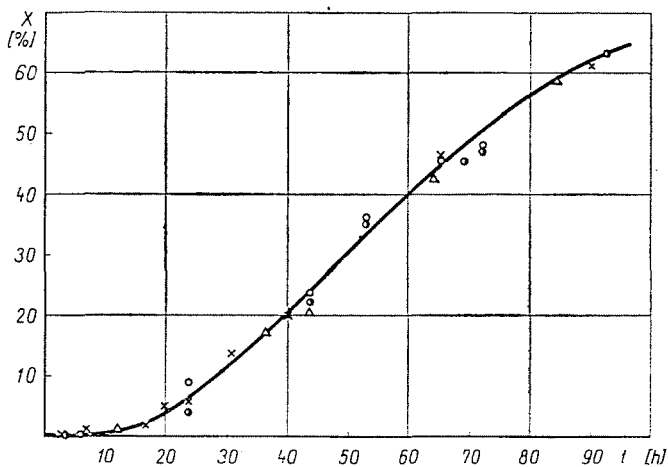
Fig. 1. Effect of secondary crystal-chemical factors on the solid phase polymerization of NVPI I modification at 30 °C. Dose rate: 1.67×10^5 rad/h. $\times$ =. Average particle size: $3.5 \times 10^2 \times 3.5 \times 10^2$ μm: $\bigcirc$ = average particle size: $28 \times 10^2 \times 4.2 \times 10^2$ μm, $\bigcirc\!\!\!\!\bullet$ = after solid phase transformation, $\triangle$ = samples crystallized at different temperatures

Fig. 2. Effect of secondary crystal-chemical factors on the solid phase polymerization of NVPI II modification at 30 °C. Dose rate: 1.67×10^5 rad/h. $\times$ =. Average particle size: $3.5 \times 10^2 \times 3.5 \times 10^2$ μm; $\bigcirc$ = averag eparticle size: $28 \times 10^2 \times 4.2 \times 10^2$ μm $\bigcirc\!\!\!\!\bullet$ = after solid phase transformation, $\triangle$ = samples crystallized at different temperatures
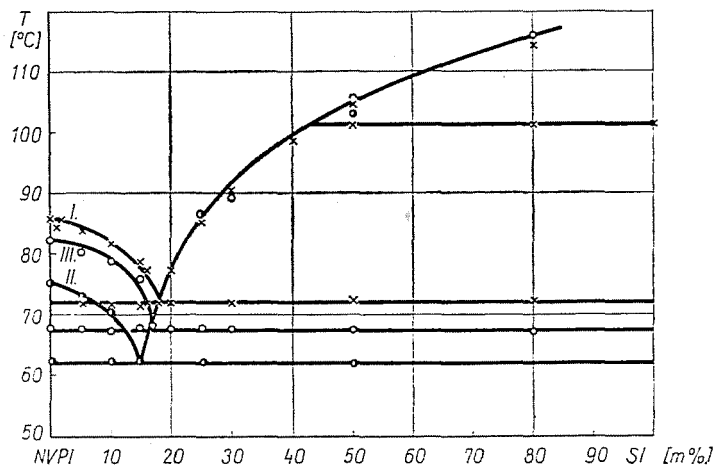
Fig. 3. Phase diagrams of NVPI modifications-SI binary systems. $\times$ = Modification I, ◑ = modification II, ○ = modification III

from melts at 50 and 70 °C, after a storage time of 1.5 month at room temperature. The samples were thereafter melted again and recrystallized (Fig. 1). The polymerization kinetics of modification II were studied on samples consisting of the above crystallites, recrystallized from isopropyl alcohol at —78 °C, 0 °C, 20 °C and 40 °C, and on samples from modification I after their transformation during storage at room temperature for 1.5 months (Fig. 2).

The polymerization kinetic data of the samples with different secondary crystal-chemical characteristics for a given modification are identical within experimental error (Figs 1 and 2), but the polymerization ability of the two modifications is significantly different.

One can therefore establish that the rate of solid phase polymerization is determined solely by the primary crystal-chemical characteristics, the role of the secondary factors being negligible.

In a further experiment series the secondary crystal-chemical characteristics of the NVPI were changed by succinimide (SI) as additive.

SI forms a binary eutectic system with all the three modifications of NVPI. The phase diagrams determined by optical polarization method are shown in Fig. 3. The dimorphous character of SI is also reflected by the phase diagram.

In Fig. 4 the diffraction angles (2Θ) vs. composition are shown for the NVPI I—SI binary system. The diffraction angles are independent of the composition, which observation proves that the primary crystal-chemical factors remain unchanged, i.e. eutectic systems are formed. At the same time, however, the secondary crystal-chemical characteristics change as a function of the composition, according to the phase diagrams, as mentioned above.
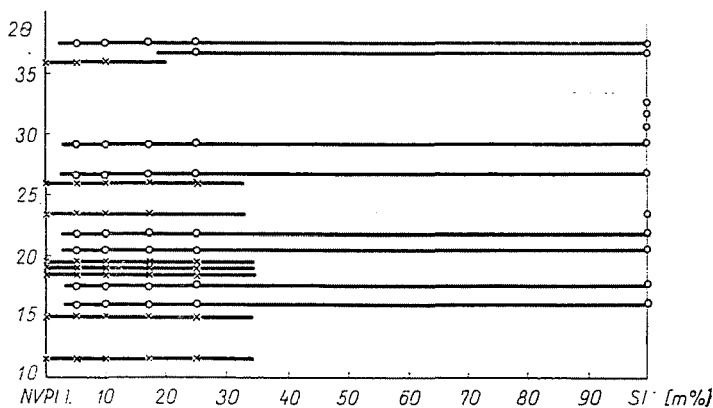
Fig. 4. X-ray diffraction angles (2Θ) vs. composition for NVPI I- SI binary systems

The course of the solid phase polymerization in the NVPI—SI system was investigated at 30 °C, at an irradiation dose rate of 1.64×10^5 rad/h, in a wide composition range (1—50 mol% SI). From the data in Figs 5—7 it is seen that the additive does not change the character of the polymerization for either of the modifications, its effect on the course of polymerization does not exceed the limit of experimental error.
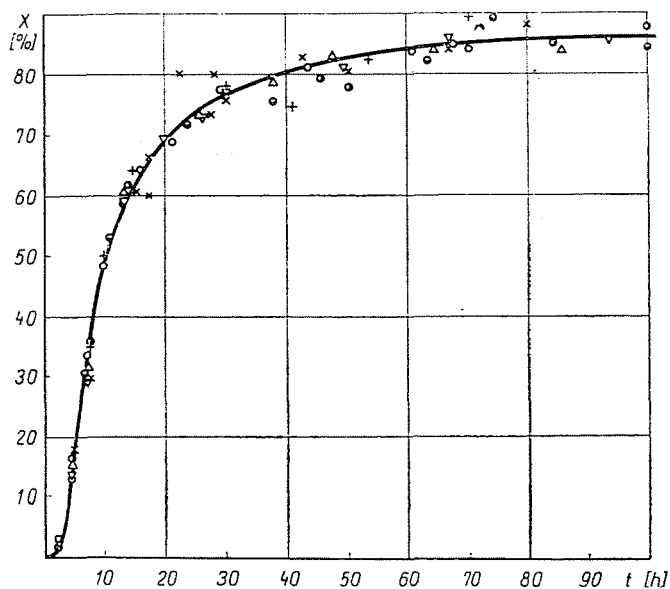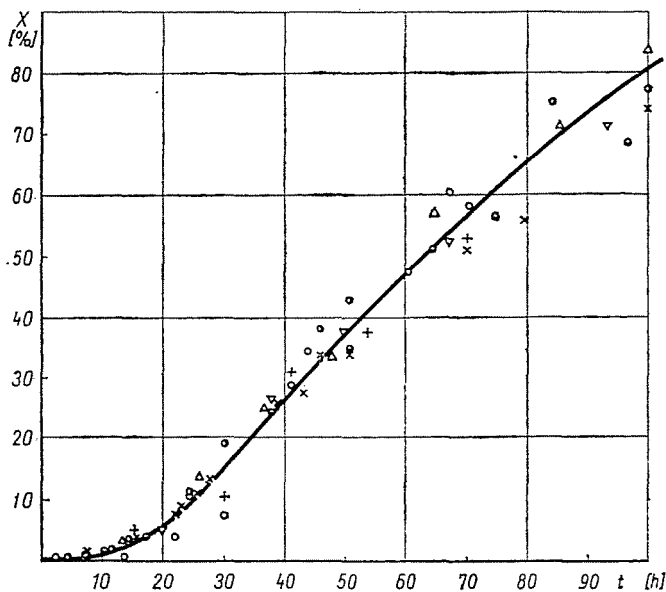

Fig. 5. Effect of the inert SI additive on the solid phase polymerization of NVPI I at 30 °C. Dose rate: 1.64×10^5 rad/h
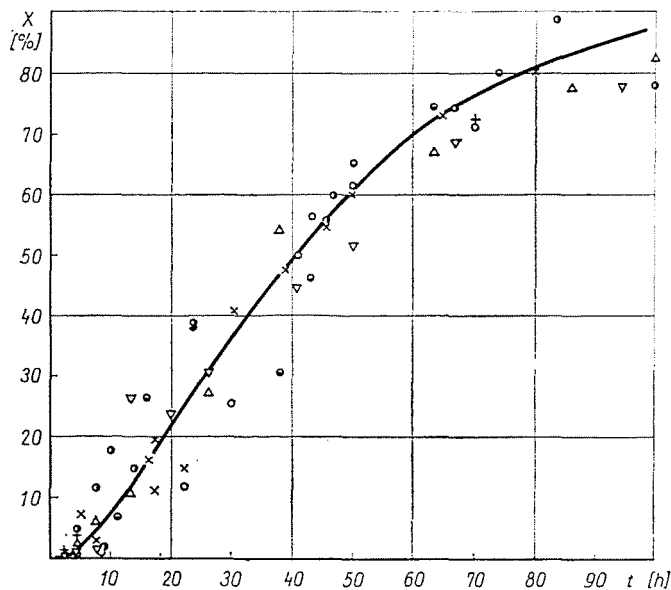Compositions of SI in mol%: ×= 0; ○ = 1.0; ◑ = 5.0; △= 10.0; ▽= 17.0; ◉ = 25.0; + = 50.0

Fig. 6. Effect of the inert SI additive on the solid phase polymerization of NVPI II at 30 °C. Dose rate: 1.64×10^5 rad/h. Compositions of SI in mol%: $\times = 0$; $\bigcirc = 1.0$; $\mathbb{O} = 5.0$; $\triangle = 10.0$; $\triangledown = 17.0$; $\mathbf{\Theta} = 25.0$; $+ = 50.0$

Fig. 7. Effect of the inert SI additive on the solid phase polymerization of NVPI III at 30 °C. Dose rate: 1.64×10^5 rad/h. Compositions of SI in mol%: $\times = 0$; $\bigcirc = 1.0$; $\mathbb{O} = 5.0$; $\triangle = 10.0$; $\triangledown = 17.0$; $\mathbf{\Theta} = 25.0$; $+ = 50.0$

In the vicinity of the melting point of the eutectic mixture (50 °C) the addition of SI caused a small increase in rate, due to mobility differences between the monomer molecules in the pure state and in a binary system, becoming apparent around the melting point of the eutectic.

The investigation of NVPI—SI systems also proves that the role of secondary crystal-chemical characteristics is negligible in the polymerization of NVPI.

Further on we studied the effect of the saturated analogue of NVPI — N-ethylphthalimide (NEPI) — on the solid phase polymerization. Contrary to expectation, NEPI does not form solid solutions of unlimited miscibility with any NVPI modifications. On the basis of the phase diagrams and X-ray diffraction investigations we established that a solid mixture of limited miscibility or a peritectic molecular complex was formed in the binary systems of NEPI and the various modifications of NVPI. Hence, NEPI can be partly incorporated into the lattice of NVPI or form a molecular complex, thus changing also the primary crystal-chemical characteristics.
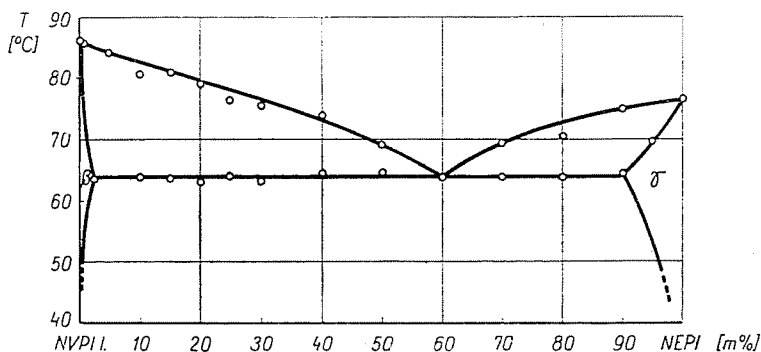

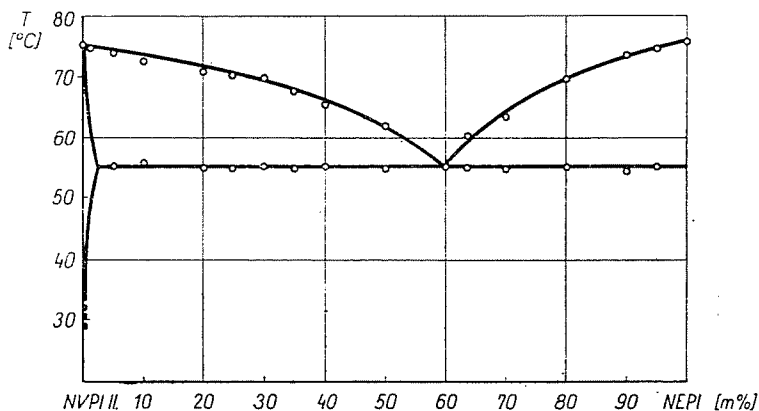Fig. 8. Phase diagram of the NVPI I- NEPI binary system

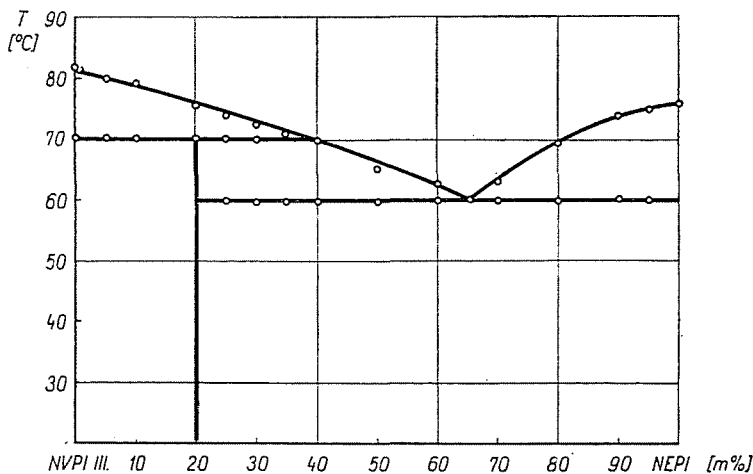Fig. 9. Phase diagram of the NVPI II- NEPI binary system

Fig. 10. Phase diagram of the NVPI III- NEPI binary system

The effect of NEPI on the solid phase polymerization of NVPI I and II could be investigated only in a narrow concentration range, because under polymerization conditions (40 °C, 1.24 rad/h) NEPI stabilized the otherwise unstable modification III.

In Figs 11 to 13 the kinetic curves for the solid phase polymerization of the various modifications of NVPI in the presence of NEPI are shown. The
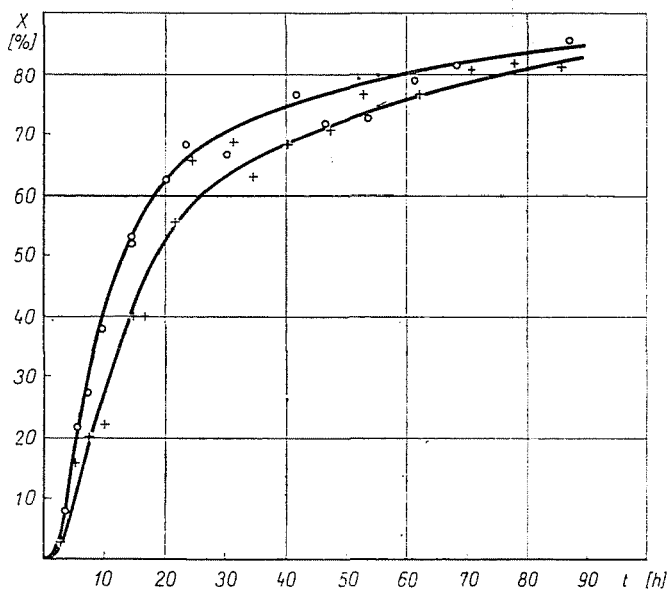

Fig. 11. Effect of NEPI on the solid phase polymerization of NVPI at 40 °C. Dose rate: 1.24 × × 10⁵ rad/h; + = 0 mol% NEPI; ○ = 1.0 mol% NEPI
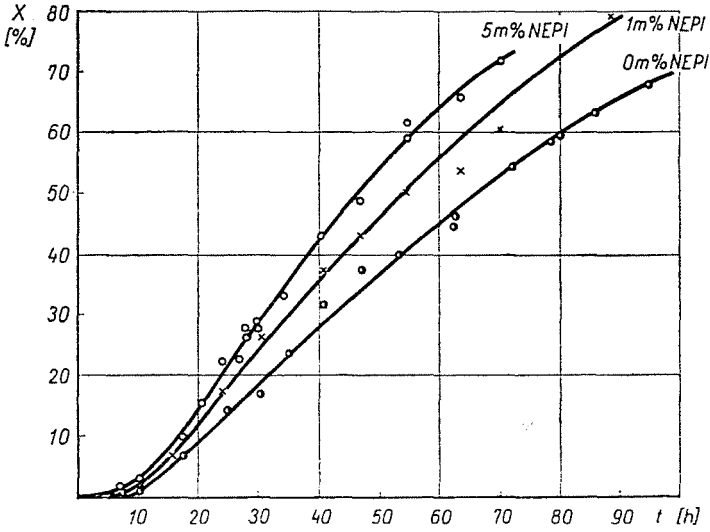
Fig. 12. Effect of NEPI on the solid phase polymerization of NVPI II at 40 °C. Dose rate: 1.24 × 10^5 rad/h. Compositions in mol% of NEPI: ◑ = 0; × = 1.0; ○ = 5.0
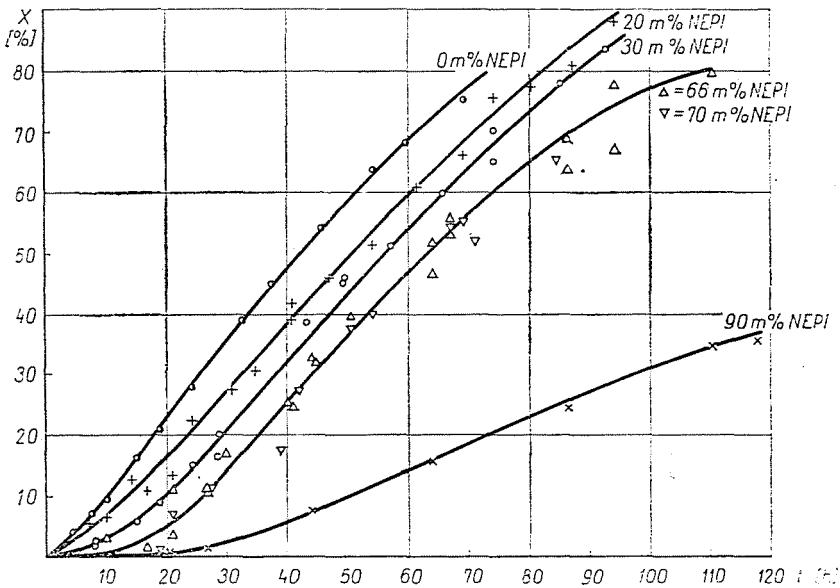

Fig. 13. Effect of NEPI on the solid phase polymerization of NVPI III at 40 °C. Dose rate: 1.24 × 10^5 rad/h. Compositions of NEPI in mol%: ◑ = 0; + = 20.0; ○ = 30.0; △ = 66.0; ▽ = 70.0; × = 90.0

data demonstrate that the solid phase polymerization of NVPI modifications I and II is accelerated by NEPI. In these cases the NEPI molecules are incorporated into the NVPI lattice, the lattice dimensions are distorted and, consequently, in the propagation step the monomer molecules have to overcome a lower energy barrier to reach the growing end of the chain.

The retarding effect with modification III is probably due to the fact that in chain propagation for the reaction between the monomer and the growing chain the preliminary decomposition of the molecular complex is needed, which increases the activation energy of chain propagation.

Summary

The effect of primary and secondary crystal-chemical characteristics has been studied on the solid phase polymerization of N-vinylphthalimide, having polymorphous modifications. It has been established that the effect of secondary crystal-chemical factors changed by varying the conditions of crystallization. it is negligible in the solid phase polymerization of the various modifications. Succinimide, forming simple eutectic system with the various modifications of N-vinylphthalimide does not influence the rate of polymerization. In the binary systems of N-ethylphthalimide and modifications of N-vinylphthalimide limited miscibility and the formation of a molecular complex have been observed, thus in this case the primary crystalchemical characteristics are modified. Addition of N-ethylphthalimide in the case of limited miscibility has an accelerating, and in the case of molecular complex formation a retarding effect.

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