

Solid-state polymerization of *N*-substituted acrylamides: 3.

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Radiation-induced solid-state polymerization at reduced temperature of homologous compounds of *N*-tert-alkylacrylamide series and of acrylamide was studied by X-ray diffractometric, gravimetric and bromine titrimetric techniques. Comparison of the kinetic curves obtained showed that the X-ray diffractometric method based on crystallinity measurements, because of disordering of the monomer, always gives higher values of conversion than do the gravimetric and titrimetric determinations. However, the general equation presented in a previous publication can be applied to the description of these curves. Deviations appear only for the conversion range above 80%, which seems to be connected mainly with the character of the method used.

Keywords Radiation-induced solid-state polymerization; X-ray diffraction; gravimetry; bromine titrimetry; kinetic curves; kinetic equation

INTRODUCTION

The first two parts of this series^{1,2} were devoted to the kinetic scheme of the radiation-induced solid-state polymerization of a series of *N*-substituted acrylamides and *N*-substituted methacrylamides. Based on a large amount of experimental material, a general equation has been derived describing the dependence of conversion on the time of irradiation. All the experiments were performed under isothermal conditions (301K) and conversions were determined by the gravimetric technique.

In the present paper, besides gravimetry, the X-ray diffraction technique³⁻⁷ and in some cases also the titrimetric measurements⁸ have been introduced. Experiments on solid-state polymerization of selected monomers of the acrylamide series were performed at reduced temperature.

The main purpose of this work is a comparison of results obtained by different methods and a description of these results by the general kinetic equation.

EXPERIMENTAL

Materials

N-tert-alkylacrylamides were obtained from acrylonitrile and corresponding tertiary alcohols according to the method described by Plaut and Ritter⁹. They were purified by repeated crystallization from methanol-water solution. A more detailed description of the synthesis was given in a previous publication¹⁰.

Acrylamide (Bruxelles r.c.b.) was purified by repeated crystallization from methanol. All monomers were dried in vacuum before use.

The list of investigated monomers, their melting points and abbreviations used in this paper are given in *Table 1*.

Polymerization

Samples of particular monomers were placed in glass ampoules, degassed at a pressure of 1.33×10^{-4} hPa and sealed. Irradiations were carried out in a ⁶⁰Co gamma source 'Gammacell 220' at dose rate at about 0.1 Gys^{-1} . Constant temperature during irradiation of a given monomer was maintained by the aid of a special thermostating equipment as described in an earlier publication¹¹. Polymerization was carried out at reduced temperature, i.e. at temperature (T_p) below the melting point (T_m) of a monomer which corresponds to the following relation:

$$T_p/T_m = 0.93$$

The reduced temperatures of all monomers studied are listed in *Table 2*.

X-ray investigations

Wide-angle X-ray measurements were performed on a powder diffractometer TuR M61 (GDR) employing copper target radiation. The incident beam was monochromatized with a bent quartz crystal. The diffracted beam obtained in the reflection mode was recorded with a Geiger-Müller counter by use of a step-scanning technique. The corrections for the non-linearity losses of the Geiger-Müller detector were determined by the method of multiple foils¹². Powder specimens for X-ray diffraction analysis were prepared in a standard way¹².

Gravimetric measurements

Monomers were separated from polymers by selected extraction using a mixture of methanol-water (1:1) for *N*-tert-alkylacrylamide series and methanol in the case of acrylamide. The isolated polymers were filtrated and dried to a constant mass under vacuum.

Table 1 Characteristics of monomers

No.	Monomer	Chemical formula	Melting point (K)	Abbreviation
1	<i>N</i> -tert-butylacrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$	400.3	NtBA
2	<i>N</i> -tert-amylacrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$	365.2	NtAA
3	<i>N</i> -tert-hexylacrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	337.1	NtHxA
4	<i>N</i> -tert-heptylacrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	335.3	NtHpA
5	Acrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$	357.5	A

Table 2 Reduced temperature and time for the radiation-induced solid-state polymerization of examined monomers

No.	Monomer	Reduced temperature ^a (K)	Reduced time ^b (h)	Reduced time ^c (h)
1	NtBA	372.0	4.60	4.39
2	NtAA	340.0	6.29	6.05
3	NtHxA	313.5	13.51	13.00
4	NtHpA	312.0	14.23	13.88
5	A	332.5	13.42	

^a Temperature of polymerization (T_p); $T_p/T_m = 0.93$

^b Time corresponding to 50% conversion measured gravimetrically

^c Time corresponding to 50% conversion measured diffractometrically

Titrimetric measurements

The content of unreacted double bonds of acrylamide in irradiated samples was determined by volumetric titration with bromine^{13,14} using an aqueous solution of potassium bromide and potassium bromate mixture in the presence of concentrated hydrochloric acid. After the addition of potassium iodide, the liberated iodine was titrated with standard sodium thiosulphate solution to the starch end point.

RESULTS AND DISCUSSION

Determination of polymer yield from X-ray diffraction

X-ray diffraction investigations have shown the crystal structure of *N*-tert-alkylacrylamide monomers^{15,16} similarly to that of acrylamide^{17,18} to be monoclinic. The angles θ and relative intensities of particular peaks on X-ray diffractograms for all monomers studied are presented schematically in Figure 1.

Since all these crystalline monomers after irradiation are converted to completely amorphous polymers, the progress of solid-state polymerization could be studied by observing the decrease in the crystalline monomeric phase and/or the increase in the amorphous polymeric phase. It seems that the decay in intensity of X-ray diffraction peaks during the course of solid-state polymerization provides a convenient technique for determining the changes in crystallinity of irradiated monomers. For this purpose

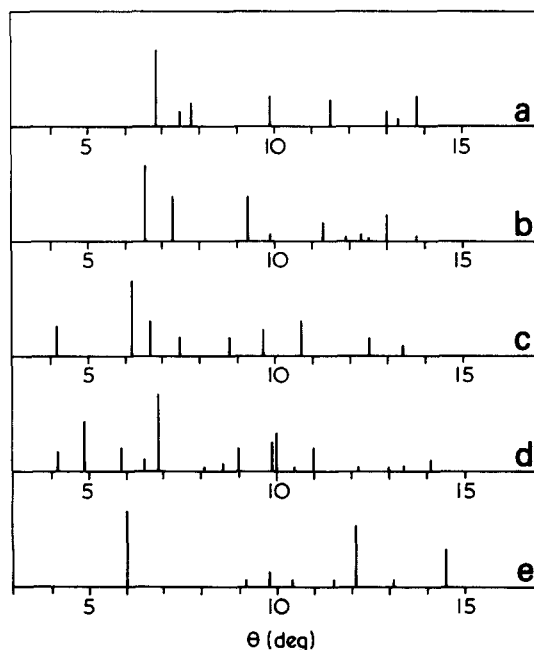


Figure 1 X-ray powder diffractograms of examined monomers (scheme of relative peak positions and intensities): (a), NtBA; (b), NtAA; (c), NtHxA; (d), NtHpA; (e), A

wide-angle X-ray diffractometry was employed. Thus, the changing content of the crystalline monomer in the samples could be estimated from diffractograms by measuring either the area of one crystalline diffraction peak or the sum of the areas of several peaks over a limited angular range, provided that the peak or the sum of the peaks represent a constant fraction of the total crystalline diffraction.

In our case both alternatives were studied and it has been found that they are practically equivalent. Therefore, the simplest procedure in taking the area of the highest peak for each monomer was selected. The angles at which these peaks occur and the corresponding Miller indices as well as the references to crystallographic data for all monomers are given in Table 3.

Table 3 Position and Miller indices of the highest peak on X-ray diffractograms of examined monomers

No.	Monomer	Highest peak		Reference
		Position, θ (deg)	Miller indices, hkl	
1	NtBA	6.82	110	15
2	NtAA	6.42	110	15
3	NtHxA	6.20	200	16
4	NtHpA	6.87	111	16
5	A	6.00	100	17, 18

The polymer yield (S_x) was calculated from the following equation:

$$S_x = \left(1 - \frac{I_s}{I_m}\right) \times 100\% \quad (1)$$

where I_s and I_m are the averaged areas under the peaks of the studied sample and monomer, respectively, after subtraction of the background.

Comparison of methods

Kinetic curves of radiation-induced solid-state polymerization of homologous series of *N*-tert-alkylacrylamides at reduced temperatures are shown in Figure 2a. Results were obtained by X-ray diffraction as well as by gravimetric methods. It is easily seen from Figure 2a that, although the general features of the curves are the same, there are

some differences in their shape due to the reactivity of particular monomers and the method used. From the more detailed analysis of these curves some regularities can be found.

First, from the viewpoint of the reactivity at reduced temperatures the curves obtained for particular monomers by X-ray diffraction and gravimetric studies are ranged in the same order. Secondly, the reactivity of the pair NtBA–NtAA as well as the pair NtHxA–NtHpA are very close to each other. This fact, known from previous investigations¹⁹, may be connected with the similarity of the crystallographic structure of these two pairs of monomers^{15,16}.

Finally, in all cases the polymer yield of the sample determined by X-ray diffractometric technique is higher than that obtained by gravimetric measurement. The curves illustrating the differences between these two methods (Figure 2b) show a pronounced maximum at high conversion.

These regularities, except for the order of reactivity of the monomers, appear especially clearly in Figure 3, where the conversion of *N*-tert-alkylacrylamides determined both by gravimetry and X-ray diffractometry is presented as a function of reduced time based on the time corresponding to 50% conversion measured gravimetrically^{11,2}. The reduced time arbitrary units for these monomers are given in Table 2.

As seen from Figure 3a for conversions up to 70% there is good coincidence between the results obtained by the same method for all the *N*-tert-alkylacrylamides studied.

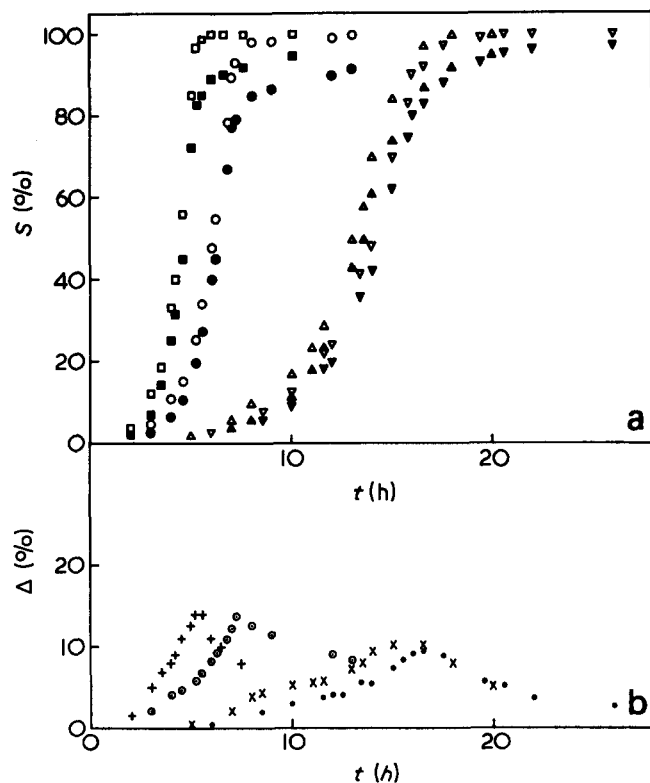


Figure 2 Radiation-induced solid-state polymerization of *N*-tert-alkylacrylamides versus time of irradiation. (a) Conversion determined by gravimetric method: ■, NtBA; ●, NtAA; ▲, NtHxA; ▼, NtHpA; and by X-ray method: □, NtBA; ○, NtAA; △, NtHxA; ▽, NtHpA. (b) Quantitative differences between conversion determined by X-ray and gravimetric methods: +, NtBA; ⊙, NtAA; X, NtHxA; ●, NtHpA

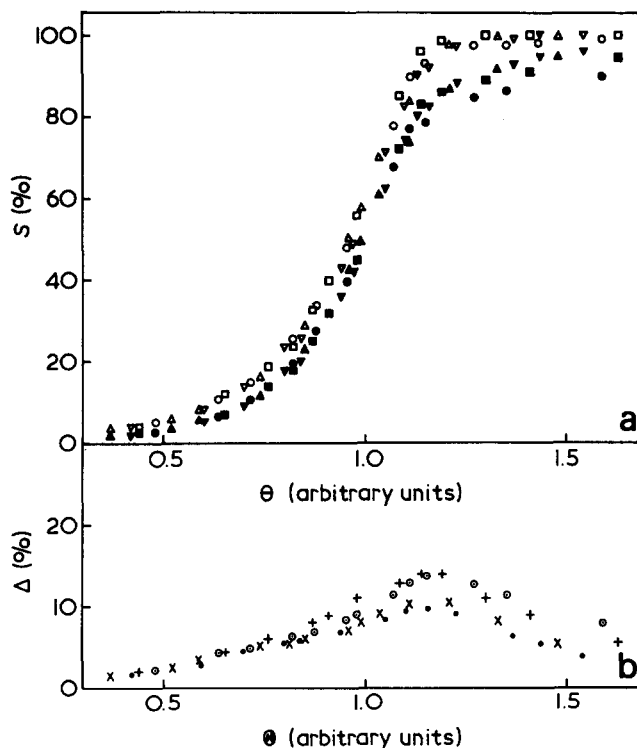


Figure 3 Radiation-induced solid-state polymerization of *N*-tert-alkylacrylamides versus reduced time based on time corresponding to gravimetric determinations. (a) Conversion determined by gravimetric method: ■, NtBA; ●, NtAA; ▲, NtHxA; ▼, NtHpA; and by X-ray method: □, NtBA; ○, NtAA; △, NtHxA; ▽, NtHpA. (b) Quantitative differences between conversion determined by X-ray and gravimetric methods: +, NtBA; ⊙, NtAA; X, NtHxA; ●, NtHpA

However, the differences between the data from the two methods used are very pronounced so that two distinctly different curves are observed.

At higher conversions the coincidence is not so strict even when the same method was used. However, the kinetic curves of the pair NtBA and NtAA are close to each other and those of the pair NtHxA and NtHpA are practically identical. This is also apparent from Figure 5 (curves A, B and C, D).

This effect is even more visible in Figure 3b where the differences between conversion measured by the use of X-ray and gravimetric techniques are presented versus reduced time. As mentioned before, all these curves form a considerable maximum at conversions of about 80% (measured gravimetrically) and of about 90% (determined diffractometrically). In principle the value of the maximum is different for each of the curves, but in Figure 3b one can easily distinguish two pairs of maxima of which the heights are very approximate to each other. The maxima of NtBA and NtAA attain the value of about 14% conversion difference, while those of NtHxA and NtHpA attain a value of about 10%.

The differences between conversions determined by X-ray and gravimetric methods may be caused by various factors.

It seems that the lower conversions obtained by the gravimetric method are connected with solubility of oligomers which may be extracted together with the monomers. This hypothesis has been partly confirmed by the use of bromine titrimetry in the polymerization progress examination of acrylamide crystals. Kinetic curves of radiation-induced solid-state polymerization of acrylamide at reduced temperature are presented in Figure 4a. Conversions were determined by X-ray, gravimetric and titrimetric methods. From Figure 4a it can be seen that the data obtained by bromine titrimetry lie between the gravimetric and diffractometric values of conversion. Quantitative differences between results obtained by particular methods as a function of polymerization time are shown in Figure 4b. The difference between the bromine and gravimetric methods suggests a partial solubility of oligomers. In support of this suggestion, the results of fractionation studies carried out by Baysal *et al.*²⁰ on polyacrylamide obtained from radiation-induced solid-state polymerization may be cited. As in our experiment, these authors isolated the polymer by extraction of residual monomer with methanol. However, the lowest fraction found had a number-average molecular weight of 9000, which proves that oligomers with lower molecular weight were extracted together with the monomer. Recently, similar observations have been made by O'Donnell *et al.*⁸ in their studies on the radiation-induced solid-state polymerization of barium methacrylate anhydrate. These authors measured polymer yields using both gravimetric and titrimetric bromine techniques. On the basis of the results obtained they concluded that oligomeric products formed during the solid-state reaction were dissolved in the water used to extract residual monomer.

On the other hand, X-ray diffractometry may give higher results due to the defects that occur in the crystal lattice of monomers under the effect of gamma irradiation and under the influence of the growing polymer chains. This interpretation is understandable taking into account the commonly accepted opinion about the close connection of crystal lattice defects with radiation-induced

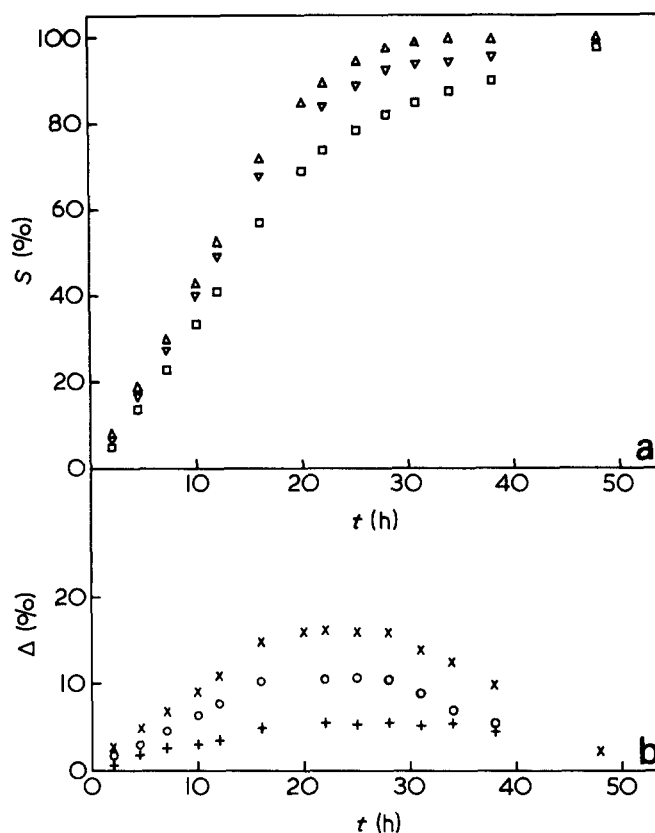


Figure 4 Radiation-induced solid-state polymerization of acrylamide versus time of irradiation. (a) Conversion determined by gravimetric (\square), bromine (∇) and X-ray (Δ) methods. (b) Quantitative differences between conversion determined by various methods: X, X-ray conversion–gravimetric conversion; \circ , bromine conversion–gravimetric conversion; +, X-ray conversion–bromine conversion

solid-state polymerization of vinyl monomers²¹⁻²³ and keeping in view the fact that as a result of lattice imperfections a portion of the X-ray scattering from the crystalline domains of a monomer is diffuse and contributes to the amorphous background. The difference between the X-ray and bromine methods in Figure 4b appears to support this view, since it may reasonably be attributed to decay in crystalline phase content owing to lattice defect formation.

It is important to realize that the crystal defects formed during crystallization, for which density is assumed to be on average the same in all irradiated samples, are not considered here, because they give rise to the diffuse X-ray scatter contributing to the amorphous background of both monomers and polymerizing samples and together with the background they are excluded from the calculations of the conversion values according to equation (1).

The shape of the curves shown in Figure 3b suggests that in the first stage of irradiation comprising a wide range of conversion the increase in the crystal defect content of the monomer is greater than the increase in the polymer content in the samples studied. The difference between these two factors increases with irradiation time to reach its maximum at the point of conversion indicated above. In the next stage the slow diminishing of the difference may be attributed to the increasing polymer content and the decreasing number of lattice defects due

to the greatly reduced quantity of crystalline monomer in the samples. In the last stage the difference continues to decrease on account of the slow but steady increase of the more and more branched polymers whereas the crystalline phase of monomer can exist only in amounts not detectable by X-ray diffraction method (100% conversion). Of course, at least in this stage the monomers remaining after the destruction of crystal structures may exist in the non-crystalline form.

Taking all this into account, it can be said that the conversion determined by gravimetric method gives the content of high molecular polymer in the sample, while the X-ray diffraction technique based on the measurements of monomer crystallinity shows the total amount of polymer, oligomer and non-crystalline monomer as well as crystal lattice defects.

The observations already referred to based on the X-ray diffractometric measurements of crystallinity may be in some measure reinforced by comparison with those of Bamford, Eastmond and Ward²⁴ and of Eastmond²⁵. These authors followed the transformation of birefringent acrylic and methacrylic acids into isotropic polymers by the change in optical retardation (i.e. optical path difference) of single crystals during irradiation with ultra-violet light. Based on this transformation, Bamford and co-workers proposed that the residual birefringence (hence the optical retardation, which is the result of the birefringence of a sample and its thickness) at any time of irradiation must be a measure of the monomer content. Indeed, the obtained plot of retardation as a function of time of irradiation for both monomers (ref. 25, p. 224, Figures 1-3, curve A) was sigmoid in shape, typical of conversion-time curves of most vinyl compounds. However, as the authors emphasize, the loss of optical retardation will not be proportional to polymer yield if some disordering of the monomer lattice is associated with polymerization. The birefringence method was used for measuring the solid-state polymerization rate both by Bamford *et al.*²¹ and by Chen and Grabar²⁶.

Although optical retardation and X-ray crystallinity are the products of different physical phenomena, they give very similar results when employed to follow the progress of the radiation-induced solid-state polymerization. This similarity arises from a common basis: the ordered space lattice of anisotropic monomers. For this reason both compared techniques are very sensitive to various kinds of crystal lattice imperfections. Therefore, it cannot be assumed that the fractional loss of retardation and X-ray crystallinity are linearly related to the percentage conversion to polymer without considering the crystal defects.

Application of general kinetic equation

Figure 5 shows two 'collective' curves of conversion plotted as a function of reduced time. However, for each of the curves the reduced time is somewhat different (see also Table 2). For the lower curve the reduced time has been determined from the time corresponding to 50% conversion measured gravimetrically. This curve is identical with the lower one presented in Figure 3a. For the higher curve the reduced time has been derived from the time corresponding to 50% conversion obtained by X-ray diffractometry. Both these 'collective' curves can be described to some extent of conversion by the general

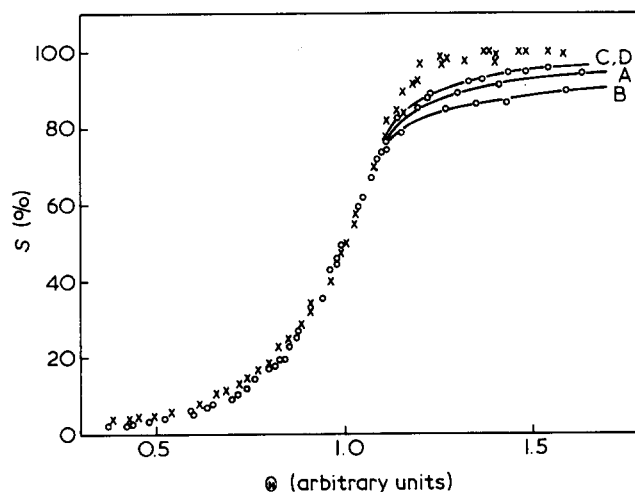


Figure 5 Radiation-induced solid-state polymerization of N-tert-alkylacrylamides versus reduced time. Conversion determined by X-ray diffractometry and reduced time (X) derived from this method. Conversion determined by gravimetry and reduced time (O) based on this method: curve A, NtBA; curve B, NtAA; curves C and D, NtHxA and NtHpA

kinetic equation reported in an earlier publication²:

$$\ln\left(\frac{S}{1-S}\right) = A_0[(\Theta - 1) + B_0(\Theta^3 - 1)] \quad (2)$$

where S and Θ are the conversion and reduced time, respectively, and A₀ and B₀ represent the constants of the equation.

Substituting for S and Θ the experimental data determined by both techniques in equation (2) after appropriate transform, two sets of equations have been obtained, i.e. one set for each technique. From these sets of equations the corresponding values of A₀ and B₀ were calculated with the aid of a computer for both techniques using the least-squares method.

Thus, in the case of gravimetric measurements the equation can be written in the following form:

$$\ln\left(\frac{S}{1-S}\right) = 3.288[(\Theta - 1) + 0.572(\Theta^3 - 1)] \quad (3)$$

while for the diffractometric technique

$$\ln\left(\frac{S}{1-S}\right) = 3.182[(\Theta - 1) + 0.443(\Theta^3 - 1)] \quad (4)$$

It should be pointed out that the numerical values of A₀ in equations (3) and (4) are very close to the value of A₀ (= 3.2803) in the equation given in the previous paper², where as the values of B₀ in these three equations markedly differ from one another. It seems that these differences may result from various conditions of temperature and dose rate under which the samples of monomers were irradiated and from various methods of determining the polymer yield as well as from a different number of polymerizing monomers which were taken into account during calculations.

As mentioned in the earlier publication², equation (2) can be presented in the form:

$$P(S) + cG(\Theta) = 0 \quad (5)$$

where

$$P(S) = \ln\left(\frac{S}{1-S}\right) \quad (6)$$

$$G(\Theta) = (\Theta - 1) + B_0(\Theta^3 - 1) \quad (7)$$

By substituting the experimental data of conversion S into equation (6) and corresponding data of reduced time Θ as well as the calculated value of B_0 for each method into equation (7) a series of values $P(S)$ and $G(\Theta)$ for particular techniques has been found. Then, the obtained values of $P(S)$ were plotted against $G(\Theta)$ as shown in Figure 6.

As can be seen from this figure, a linear relation of $P(S)/G(\Theta)$ is maintained within a wide range for both techniques. Some small deviations from linearity are observed at low $G(\Theta)$ values and much larger ones, however, at high $G(\Theta)$ data corresponding to conversions above 80%. The deviations in Figure 6 clearly appear to be dependent on the method applied. The plots $P(S)/G(\Theta)$ obtained from the gravimetric measurements show the departure towards lower values of $P(S)$, while those based on X-ray diffraction data in contrast indicate the departure in the directions of higher values of $P(S)$. This departure from linear $P(S)/G(\Theta)$ dependence particularly at its upper part may be explained in the following way.

In the case of gravimetric measurements, it seems that equation (3) is not obeyed accurately on account of the

considerably lower polymerization rate resulting from the greatly reduced quantity of the monomer at high conversions.

In the case of diffractometric observations, the main reason for the deviations may be the rapid increase in the crystal defect content of the small amount of monomer remaining in the samples. Similar observations during radiation-induced solid-state polymerization of acenaphthylene have been made by Hardy *et al.*⁵ These authors have found that the polymer yield of this monomer determined by X-ray diffraction (but in another way than in our experiment) at low and middle conversions is equal to the yield measured gravimetrically. However, at higher conversions the polymer yield derived from X-ray data increases faster than that obtained by gravimetric method.

It should be noted that the polymer yield at very small conversions (at about 3%) cannot be determined from the X-ray crystallinity because of the rapid increase in the crystallinity of irradiated monomers under study in this region. This phenomenon, which has not been sufficiently explained yet, was also observed with acrylamide, methacrylamide and *N*-vinyl carbazole by Pékala *et al.*⁷

CONCLUSIONS

Comparison of the methods used leads to the conclusion that X-ray powder diffractometry based on measurements of monomer crystallinity seems to add to the actual polymer yield the value corresponding mainly to the defect content of the monomer, at the same time indicating a progressive destruction of the crystalline phase in the sample, while gravimetry seems to subtract from the true polymer yield the weight of soluble oligomers joined to the extracted monomer.

Similarity between the results determined from X-ray crystallinity and those measured from optical retardation also indicates that the disordering of the monomer lattice accompanying the radiation-induced polymerization plays an important part in obtaining the kinetic data of investigated vinyl monomers.

The general kinetic equation derived for isothermal conditions of irradiation can also be applied to solid-state polymerization performed at reduced temperatures. The directions of deviations from the obtained linear relation of $P(S)/G(\Theta)$ at its upper part corresponding to conversions higher than 80% are likely to be connected mainly with the method applied.

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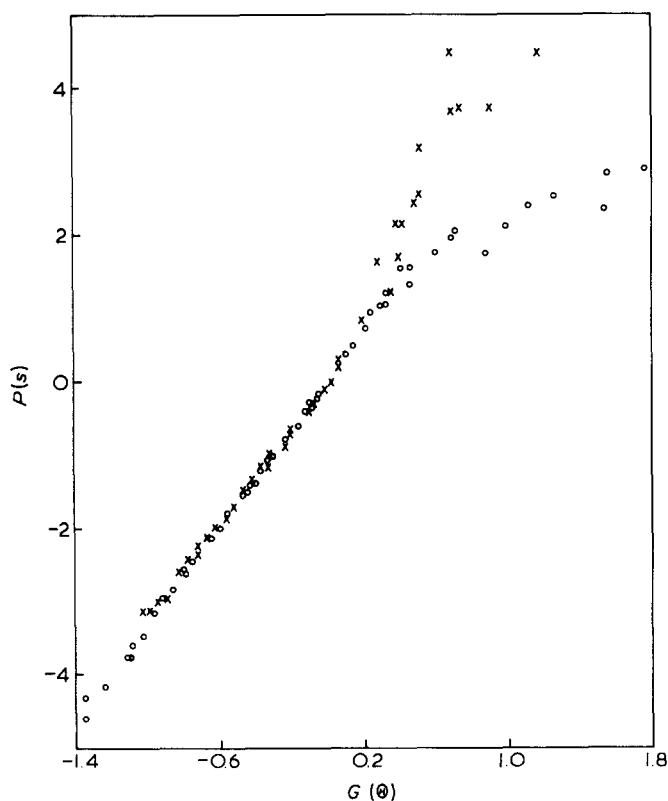


Figure 6 Relation between $P(S) = \ln[S/(1-S)]$ and $G(\Theta) = (\Theta - 1) + B_0(\Theta^3 - 1)$: X, for X-ray determinations, $B_0 = 0.443$; O, for gravimetric measurements, $B_0 = 0.572$

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