Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Faucitanot, A. and Adler, G.(1970) 'Annealing and Recrystallization in the Solid-state Polymerization in Solid Solutions of Methacrylamide and Isobutyramide', Journal of Macromolecular Science, Part A, 4: 2, 261 — 275
To link to this Article: DOI: 10.1080/00222337008063147
URL: http://dx.doi.org/10.1080/00222337008063147

J. MACROMOL. SCI.–CHEM., A4(2), pp. 261-275, March, 1970

Annealing and Recrystallization in the Solid-State Polymerization in Solid Solutions of Methacrylamide and Isobutyramide*

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SUMMARY

It is shown that lattice parameter changes that reflect the composition of the unpolymerized material occur during the solid-state polymerization of methacrylamide in solid solution with isobutyramide. In addition, phase changes also occur as is required by the phase diagram of the system. These results indicate that annealing and recrystallization must play an important role in this reaction and probably in other solid-state polymerizations. It is also likely that these effects are among the parameters that are important in determining the rate of solid-state polymerization.

It has been shown that, during the polymerization of acrylamide, the polymer nucleates as a second phase at an early stage of the reaction [1, 2, 3]. Further reaction then occurs at the monomer-polymer interface.

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*This work was performed under the auspices of the U.S. Atomic Energy Commission.

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Acrylamide forms solid solutions in all proportions with propionamide [4]. It has been shown that these solid solutions give unexpectedly high yields of polymer even when the acrylamide is so dilute that on the average the acrylamide molecules are relatively isolated [5]. This is most easily explained by assuming that acrylamide molecules that happen to be close enough to react do so, and these can be considered as the nuclei of a polymer phase. There results a net shrinkage in volume which induces some lattice strain, but more importantly, it facilitates diffusion in the immediate region. The fact that the nucleation sites tend to occur at defects such as dislocations also affects the mobility of the molecules. The propionamide is apparently relatively insoluble in the polymer and would concentrate at the monomer polymer interface as the reaction proceeds. Then, since the yields of polymer are high and molecular weights relatively large, it seems obvious that diffusion and therefore recrystallization and annealing must have taken place at the reaction temperature. It seemed to us that an x-ray diffraction study of this process would lead to a better understanding of polymerization and other solid-state reactions. The system methacrylamide-isobutyramide is particularly favorable for such work. The phase diagram shows two eutectics and an intermediate phase which is able to form solid solutions with either component over a limited range of composition. It was shown a number of years ago that methacrylamide polymerizes in the solid state [6]. Therefore if we choose a composition in the proper range, we could check for annealing and recrystallization by observing phase changes and shifts in lattice parameters.

EXPERIMENTAL

The methacrylamide and isobutyramide were recrystallized twice from acetone. The solid solutions were prepared by weighing and mixing the required amounts, heating the mixture above the melting point, and then shock cooling at -15°C immediately. Finally the material was ground in a mortar and pestle. Blank tests with unirradiated material showed that no polymer was formed during this procedure.

Part of the material was then packed into flat, rectangular Bakelite slides which had a shallow well cut into them. A sheet of 1 mil thick Mylar was then glued over the face. These were used for x-ray diffraction. Some of the slides had a small amount of NaCl mixed with the material for use as an internal standard during diffraction analysis.

The rest of the material was sealed into glass tubes under vacuum.

The slides and the glass tubes were irradiated in a Co^{60} gamma source to the required dose. For most samples a dose rate of 0.78 MR/hour and an irradiation temperature of 23°C was used. For a few experiments a dose rate of 7.9 MR/hr and a temperature of 30°C was used. Dosimetry was determined by the Fricke method [7].

The slides were mounted in a General Electric XRD-3 diffraction unit and the diffraction patterns were taken with a counter-diffractometer. The slides were then usually reirradiated to a higher dose and the procedure repeated. The degree of conversion was determined by isolating the polymer with methanol and drying to constant weight. This data was then used to plot the yield vs d-spacing curves for selected diffraction peaks.

It will be shown in a subsequent publication [8] that oxygen influences the rate of polymerization. Air was certainly present when the slides were irradiated. However, we took the diffraction patterns of a number of samples that had been irradiated under vacuum and also measured the polymer yield for samples irradiated on the slide. Though the polymer yield vs radiation dose curves were somewhat displaced for these two irradiation conditions, the yield vs d-spacing curves for the diffraction peaks were identical. We therefore assumed the above outlined procedure for convenience.

The phase diagram of the system was determined both by x-ray diffraction and by thermal analysis using a Perkin-Elmer model 1-B differential scanning calorimeter. The samples for the latter procedure was prepared by slow cooling of the melt with stirring. In this case 0.1% hydroquinone was added to prevent the small amount of thermal polymerization that occurred during the prolonged heating. This was found to have no effect on the phase diagram.

RESULTS AND DISCUSSION

The calorimetrically determined phase diagram (Fig. 1) makes it obvious that, unlike the acrylamide-propionamide system [4], the methacrylamide-isobutyramide system does not form solid solutions over the entire concentration range. Instead there seems to be two eutectics at approximately 45 and 78% methacrylamide, and an intermediate phase containing both components, which we shall call B. The B phase has a congruent melting point at about 65% methacrylamide. This may indicate the formation of some sort of complex.

The B phase can exist over a relatively wide range of composition. In other words, it can accommodate an appreciable amount of either methacrylamide or isobutyramide as a solid solution. The stoichiometry of the

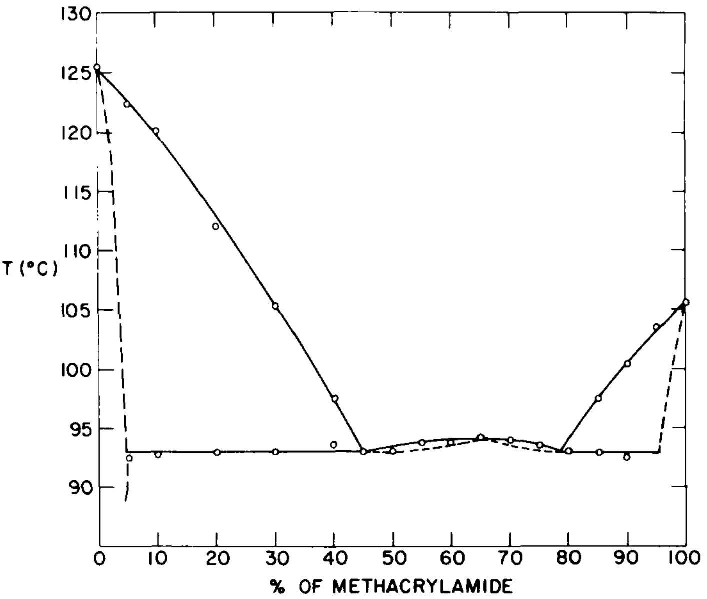

Fig. 1. Phase diagram of the methacrylamide-isobutyramide system as determined by differential scanning calorimetry.

phase is therefore variable. On the isobutyramide side of the phase diagram, the situation is quite different.

The isobutyramide structure (phase I) can accommodate little methacrylamide in its lattice. Therefore phases I and B occur together over a wide range of compositions. A similar situation exists on the methacrylamide side where phase B and methacrylamide (phase M) subsist together over a wide composition range.

This picture is supported by the x-ray diffraction data taken from unirradiated samples. Figure 2 shows selected d spacings obtained from relatively low-angle reflections of each of the phases. Between about 45 and 78% only the lines from phase B were generally present and the d spacing varied linearly with composition, as is expected for a solid solution. Below 45% the B spacings remained relatively constant but the lines decreased in intensity as the amount of methacrylamide was decreased. On the other hand, the lines from phase I, except for a possible small initial change remained constant in d spacing until the line disappeared completely about 45% methacrylamide. This is the behavior expected for a region where two phases exist simultaneously.

Above 75% methacrylamide the d spacing of the B lines were again

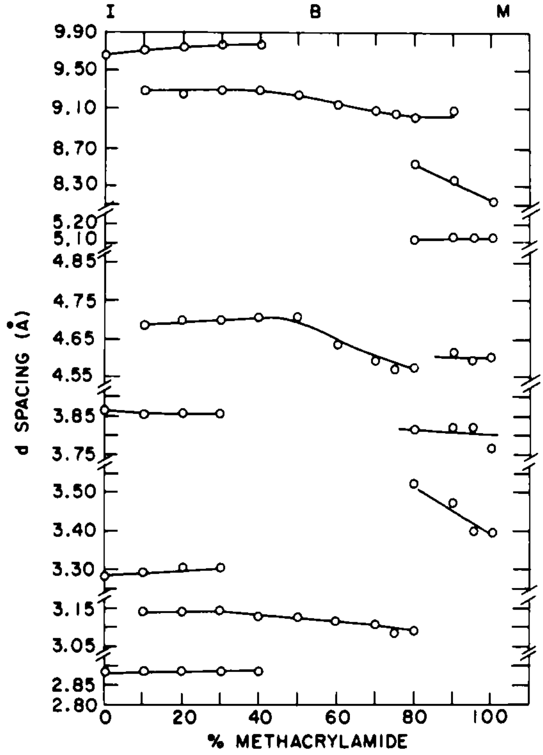

Fig. 2. d Spacing of methacrylamide as a function of composition in quenched solid solutions at 25°C.

constant until they disappeared. The M lines began to appear at about 78% methacrylamide simultaneously with the B lines, again indicating a two-phase region. However the M line varied in d spacing over the whole region. This is probably due to a metastable phase composition which was frozen in when the material was quenched at -15°C. It should also be noted that the scatter of data was somewhat larger in this area.

We concentrated on the low-angle peaks during the rest of the experimental work since these were relatively intense, easy to measure, and appeared to be sensitive to changes in composition.

The diffraction patterns of pure methacrylamide samples irradiated to various doses, and therefore having varying degrees of polymerization, show negligible difference in the d spacings. The intensity of the diffraction line due to crystalline monomer simply decreases with conversion until it disappears at complete polymerization. At the same time, the very broad diffuse pattern due to amorphous polymer increases. The line width of the diffraction peaks increase somewhat during polymerization, probably due to build-up of strain and increase in the mosaic spread of the crystal. The behavior of pure methacrylamide is thus seen to be very similar to that of acrylamide [1]. The polymerization of methacrylamide also involves a two-phase mechanism where the polymer nucleates as a second phase at an early stage of the reaction. The bulk of the reaction would then occur at the monomer-polymer interface and not deep within the crystal lattice.

In a solid solution of methacrylamide and isobutyramide the situation and therefore the diffraction behavior is necessarily somewhat more complex. The isobutyramide does not enter into the reaction. As a result, the unpolymerized phase must get richer in this compound. If annealing and recrystallization takes place it would become apparent in the diffraction pattern. For a composition in the range of phase B, if the rate of recrystallization and annealing are high enough compared to the rate of polymerization, the d spacing should change so as to reflect the composition of the remaining material after the polymerized methacrylamide has been subtracted. This means a shift of the relevant reflections towards smaller angles (larger d spacing) would be observed. Near the phase boundary (~45% methacrylamide) we would expect to see the initial appearance of the I phase. The B phase lines from this point on would remain constant in d spacing but with decreasing intensity. If no annealing were taking place, the lines should be constant in d spacing but would probably get broader due to the strain and breakup of the crystals. Since, in our case, the polymerizations were carried out some distance below the melting point, intermediate behavior would be expected unless the annealing rate became one of the parameters limiting the polymerization rate.

To check this, material in the B phase range was irradiated at 25°C so that polymerization occurred during irradiation. The results for the most intense reflection are given in Fig. 3. Three things are apparent. The d spacing does change in the direction expected from depletion of methacrylamide. Secondly, there is a prolonged initial period where there is little change. This suggests that the polymerization reaction either requires a long induction period or an appreciable amount of strain must be built up before annealing becomes relatively rapid. It is known that the solid-state polymerization of methacrylamide has a long induction period (see Fig. 8). Nucleation of the polymer phase is probably involved, but strain build-up may play at least some role in this phenomenon.

Finally, it is apparent that the d spacing can increase beyond about 9.3 Å, where we would expect from our phase diagram that the d spacing becomes constant and the I phase nucleates. It means we have achieved

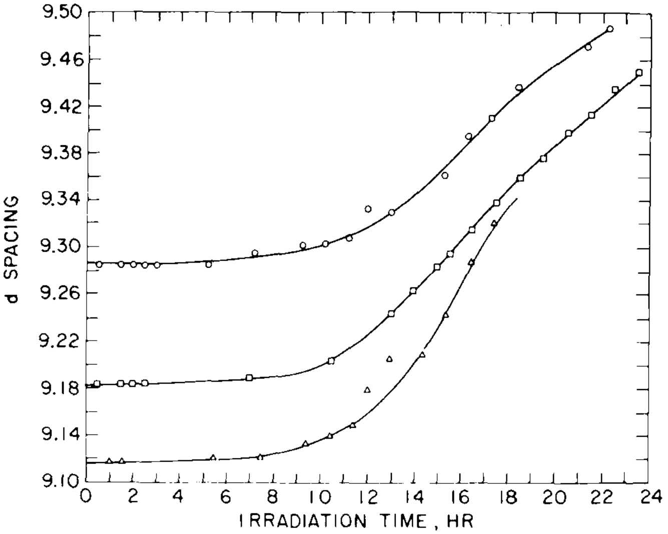

Fig. 3. Variation of d spacing in the β phase as a function of irradiation time during the in-source polymerization of various solid solutions of methacrylamide and isobutyramide. Radiation dose rate 0.79 MR/hr. (○) 50% methacrylamide. (□) 60% methacrylamide. (△) 70% methacrylamide.

a metastable configuration. This is possible if the activation energy for annealing is less than that for nucleating the I phase or if the rate of growth of the I phase is low. It is suggestive that we have gotten spacing as high as 9.47 Å by varying quenching temperature in formation of these solid solutions. The phase boundary value of 9.30 Å which we obtained previously probably does not accurately reflect the equilibrium value since it was also obtained from quenched solid solutions.

In Fig. 4 are reported the d spacing change for a 50% solid solution as a function of the percent isobutyramide left in the system after partial polymerization of the methacrylamide. The results are plotted for two dose rates which differ by a factor of ten. For comparison we included d spacing shift as a function of composition for the quenched solid solutions of various composition in which no polymerization has occurred. This was extrapolated into the metastable region (beyond the phase boundary). We see that the shift for the polymerized material is roughly comparable to that of the unreacted solid solutions. Initially the polymerizing material changes more slowly than expected but then it becomes more rapid. This difference could reflect either a build-up of strain necessary before annealing becomes reasonably rapid or a limited solubility

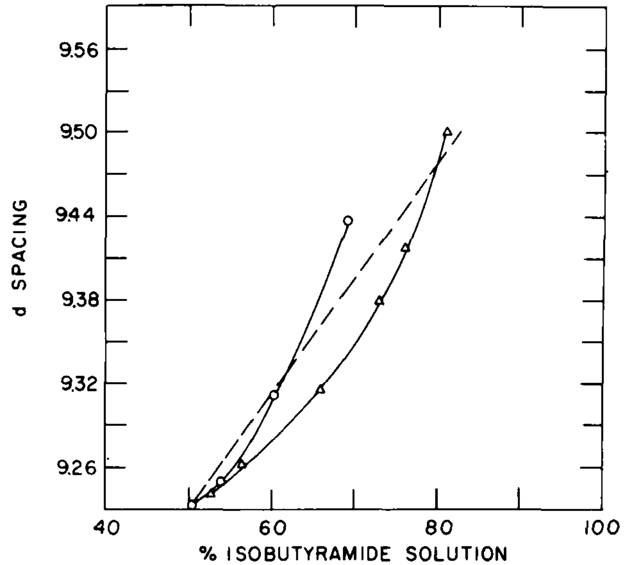

Fig. 4. Variation of d spacing in a solid solution initially 50% isobutyramide as a function of the percent isobutyramide remaining after removal of methacrylamide by polymerization. (○) Dose rate 0.79 MR/hr. (△) Dose rate 7.9 MR/hr. The dashed line represents the extrapolated value of the d spacing as a function of composition in unirradiated solid solutions.

of isobutryamide in the polymer phase. The former is probably more important. Also, the material irradiated at the lower dose rate changes somewhat more rapidly as a function of composition than the other. This may be due to differences in annealing time. Since the lower dose rate sample took roughly ten times as long as the other to achieve a similar change in composition, it had a longer time to anneal.

When a melted mixture of 90% methacrylamide and 10% isobutyramide is quenched, the diffraction diagram shows the presence of both the B phase and the M phase, the latter having the structure of methacrylamide. In Fig. 5 part of the diffraction diagram and its change with irradiation time are shown. The peaks due to the various phases are labeled. As can be seen, the over-all intensity of the peaks grows less with time. This is because 90% of the material (the methacrylamide) is progressively removed as amorphous polymer which just adds to the apparent background. The M peak loses intensity and disappears before the B peak. At the same time its diffraction angle shifts 0.16° towards smaller angles (increased d spacing). The B phase also shifts about 0.17° and finally disappears. At the end we

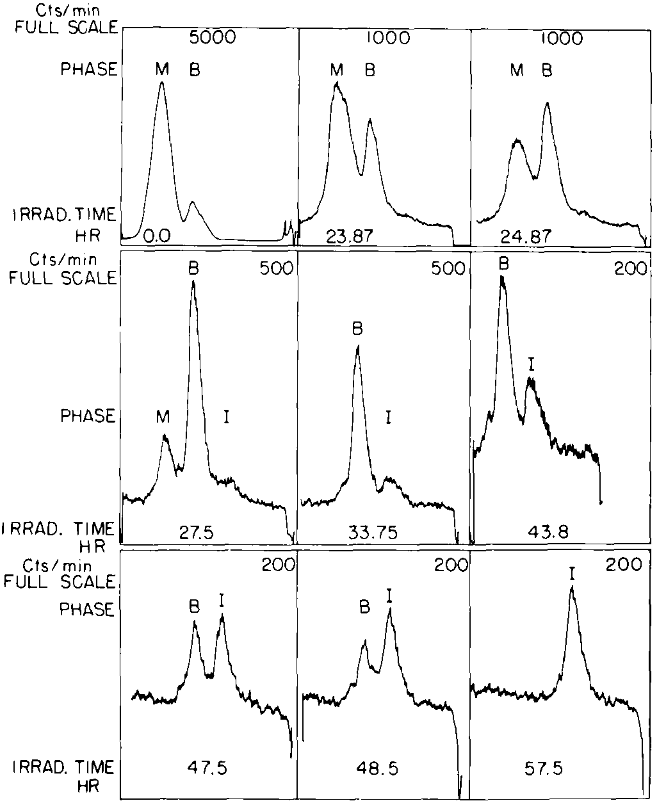

Fig. 5. Diffraction diagrams showing intensity changes in low-angle reflections of a solid solution initially 90% methacrylamide. Nickel filtered copper radiation used.

are left with a small peak due to the residual I phase which was not there originally. These changes in intensity are shown in Fig. 6. The very rapid decrease of the M peak is due both to polymerization and to conversion to B phase as the amount of available methacrylamide becomes less. As the M line finally disappears, there is a slight temporary increase in the B line, probably due to recrystallization of M to B phase. Simultaneously through most of this time, there is a decrease in the B phase since its methacrylamide is being depleted and it, in turn, changes to the I phase.

Till now we have spoken only of systems which were allowed to polymerize in the irradiation source while being irradiated. Methacrylamide will also polymerize when removed from the source. This is the so-called post-polymerization reaction. Figure 7 shows the change of d spacing as a

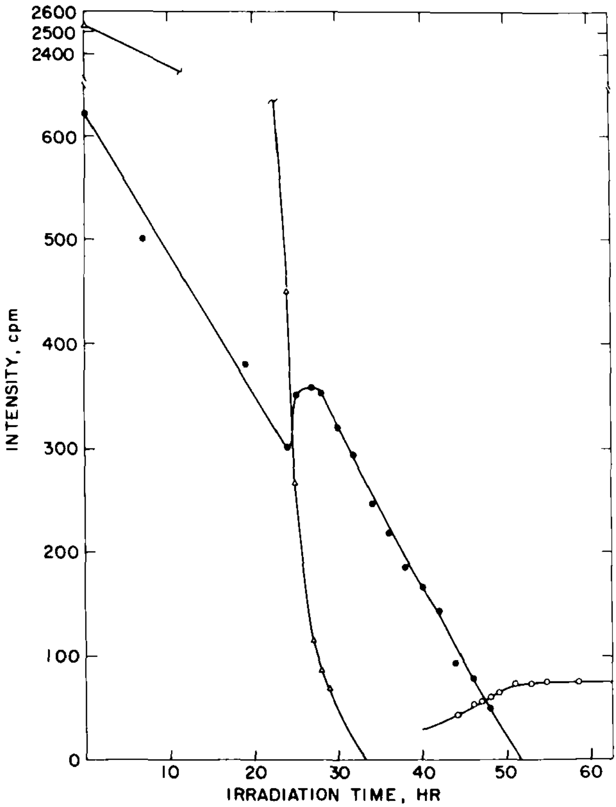

Fig. 6. Intensity changes as a function of irradiation time in low-angle reflections in a solid solution initially 90% methacrylamide. Dose rate 0.79 MR/hr. (△) M-phase reflection. (●) B-phase reflection. (○) I-phase reflection.

function of reaction time in post-polymerization. As can be seen, the d spacing increases as expected. The increase goes beyond the limit of the phase boundary as shown in Figs. 1 and 2, indicating a metastable solid solution supersaturated in isobutyramide. The curve finally breaks, going to a lower d spacing which then appears to remain relatively constant. This break probably occurs concommitantly with the appearance and nucleation of the I phase.

Finally in Fig. 8 we show the polymer conversion curves for the in-source polymerization of various solid solutions. It is evident that the conversion curves for the solid solutions all have a smaller induction time for

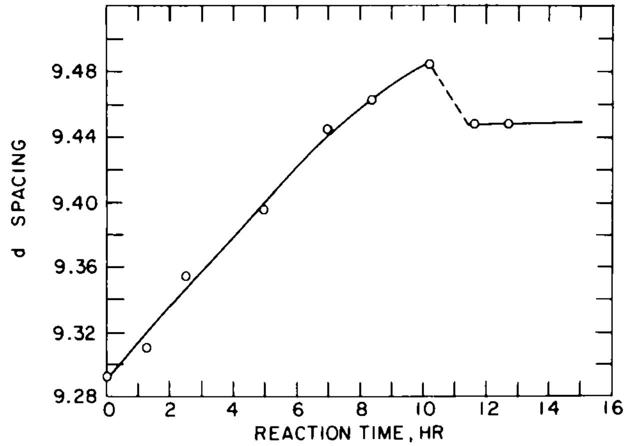

Fig. 7. d Spacing change as a function of reaction time during the post-irradiation polymerization of a 50% solid solution of methacrylamide. Total dose 32 MR.

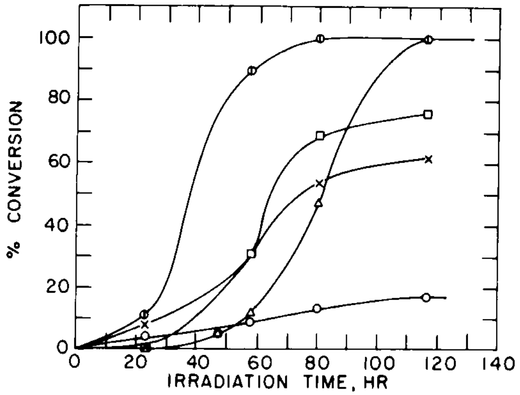

Fig. 8. Conversion of methacrylamide to polymer during in-source polymerization of various solid solutions. Dose rate 0.79 MR/hr. (△) 100% methacrylamide. (⦶) 80% methacrylamide. (□) 50% methacrylamide. (X) 30% methacrylamide. (○) 5% methacrylamide.

polymerization than pure methacrylamide. In so far as the induction period is a reflection of polymer nucleation, this would suggest that nucleation occurs more easily in the solid solutions. It can also be seen that the initial polymerization is more rapid in the solid solutions. This is most evident in the 80% methacrylamide solution. There seem to be several possible explanations for this. The material is almost entirely B phase. It might be argued that this is the B-phase material richest in methacrylamide and the B-phase structure somehow facilitates polymerization. The other argument is that during reaction the composition of the nonpolymerized matrix changes and this results in phase changes and implies some sort of motion and rearrangement of the molecules. It has been shown by several workers (for example, see Ref. 9) that the rate of polymerization increases rapidly during a phase change. A third factor, especially in dilute solid solutions, might be the presence of the minor component which in a sense is a defect in the lattice and perturbs it. There must be stresses, strains, and lattice distortions in the vicinity of its molecules, and these, along with the dislocations and other defects already present, may facilitate nucleation and diffusion. It is difficult, at present, to specify which of these three factors is responsible. Probably all three play some role. At present we are inclined to believe the phase change mechanism is the more important.

Something should be said here about the data obtained. In a quantitative sense, it is reproducible within rather wide limits when samples prepared at different times are compared. This is common in solid-state reactions and is especially understandable in organic solid solutions where quenching rates, defects, and impurity content, small temperature fluctuations, recrystallization, and other experimental parameters which can be controlled only with great difficulty are involved. However, each set of samples showed good internal consistency and in all cases the trend of the data was the same so there can be little doubt that the results are at least qualitatively correct.

CONCLUSIONS

Polymerization is a reaction that requires a constant supply of reactive molecules at the reaction site. In a solid solution where only one of the components is reactive, this would imply a depletion reactive molecule and a concentration of unreactive ones which would soon end the reaction unless some mechanism were available to bring fresh molecules to the reaction site. Previous work with solid solutions of acrylamide in propionamide [5] has shown that nearly all the acrylamide is polymerized to reasonably high molecular weight even in rather dilute solid solutions. The present work on methacrylamide-isobutyramide system shows there is a constant change in lattice parameter during polymerization which reflects the change in composition of the residual solid solution. This shows the system is constantly annealing and probably recrystallizing at the monomer-polymer interface. Annealing and recrystallization imply some sort of diffusive motion must occur within the lattice, at least at reaction temperatures. Thus, we have a means not only for relieving stresses and strains which are built up during reaction, but also for allowing reactive molecules to diffuse to the active site so that the reaction can go to completion. It cannot be argued that if the unreactive component is soluble in the polymer there would be no need for diffusion. First of all, the unreactive component does not seem to be soluble. Secondly, there would then be no need for the lattice parameters or, in the case of the system here considered, the phase of the unreacted material to change.

Annealing is probably a concommitant of all the solid-state polymerizations, at least those that go to completion. It is needed to relieve the build-up of stresses, if for no other reason. In solid solutions, at least, it is needed to bring up fresh material to the reaction site. It is quite possible that some of the reactions that do not go to completion fail to do so because the stresses which can build up and inhibit the reaction are not annealed rapidly enough. It is also reasonable that annealing is one of the factors that determines the reaction rate, and through it, molecular weight distribution in these systems.

It was also shown that polymerization in the methacrylamide-isobutyramide system can be more rapid with a shorter induction period than in pure methacrylamide. The phase changes which occur during polymerization as well as the possibility of more rapid diffusion in the solid solutions can be invoked to explain this. The phase change involves more extensive molecular motion and allows more rapid reaction during the process. This is consistent with previous observations [9]. It has been noted that for mixtures of two monomers, the rate of reaction is often most rapid at the eutectic composition [10]. This effect has sometimes been attributed to the small size and consequent large surface and interfacial area of the crystallites in such a system, especially if reaction were to occur more rapidly at such surfaces. Very probably this is at least part of the explantaion in many cases. The work recorded here suggests another mechanism is also involved. If one component of the solid solution polymerizes more rapidly than the other, then the crystal becomes depleted. As a result a phase change can occur if the phase diagram requires it.

The phase change would be accompanied by rapid polymerization. The observations recorded here may also help explain the effects of inert additives in some cases. For example, Fadner et al. [4] have shown that a small amount of acetamide will accelerate the polymerization of acrylamide. Acetamide has a limited solubility in acrylamide. It seems reasonable that as the polymerization proceeds and the concentration of acetamide in the residual material increases, a phase change occurs with accompanying rapid polymerization. It is suggestive that propionamide, which forms solid solutions in all proportions with acrylamide, does not cause a comparable increase in polymerization rate.

It has been shown by x-ray diffraction techniques in this communication that annealing, recrystallization, and phase change are very important factors governing polymerization in the methacrylamide-isobutyramide system. This is probably true in all solid-state polymerizations. The diffraction techniques can provide an important adjunct in studying reaction mechanisms in these systems. Finally, it should be mentioned that polymerization in solid solutions can provide a significant insight into the study of such solid-state problems as annealing and phase stability since the reaction removes one component from the system without the necessity of dissolving or melting.

ACKNOWLEDGMENT

A. Faucitano wishes to acknowledge the receipt of a NATO fellowship to pursue this work.

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Accepted by editor August 5, 1969
Received for publication September 17, 1969