

1-1-1997

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USANMAZ, Ali (1997) "Crystal Structure Effect in Radiation-Induced Solid-State Polymerization of Acrylamide," *Turkish Journal of Chemistry*: Vol. 21: No. 4, Article 11. Available at: <https://journals.tubitak.gov.tr/chem/vol21/iss4/11>

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Crystal Structure Effect in Radiation-Induced Solid-State Polymerization of Acrylamide

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Received 16.5.1997

Crystal structure of acrylamide at -150°C was studied to understand the role of the crystal structure on the reaction mechanism of radiation-induced polymerization in the solid-state. Acrylamide crystallizes in the monoclinic unit cell with the unit cell parameters as ; $a=828.0(2)$ pm, $b=578.0(4)$ pm, $c=974.9(2)$ pm, $\beta=119.62(4)^{\circ}$, space group =P $2_1/c$, $Z=4$ molecules/unit cell, $d_x = 1.165$ g/cm³. From the results of the structural data a polymerization mechanism in the solid-state is suggested. The radiation damage in single crystal of acrylamide was also investigated in detail. The result showed the formation of the amorphous polymer, that phase separated from the crystalline monomer. The post polymerization proceed at the interface of polymer-monomer up to 100% conversion.

Introduction

The radiation, induced polymerization in the solid-state have been extensively studied in late 1950s and 1960 s and there are many publications and review articles¹⁻¹¹ on the subject. However, the limited information about the structure of monomers used in this area raises many problems and difficulties. Since these type of monomers are radiation sensitive, their structure determination at room temperature in most cases is not possible. Thus, the structure determination has to be carried out at low temperature which have many experimental problems. In our laboratory, we have been investigating the relation between crystal structure and solid-state polymerization mechanism of some monomers of different structure and chemical natures¹²⁻¹⁶. However, we have carried out the most detailed work on acrylamide¹⁷⁻¹⁸.

The radiation-induced solid-state polymerization of acrylamide was studied for the first time at Polytechnic Institute of Brooklyn and Brookhaven National Laboratory, pioneered by Adler, Baysal, Morawetz, *et al*^{1,4-10}. A crystalline polymer was expected to be obtained in a solid-state polymerization because of limited mobility of molecules in the solid matrix. However, the polymer was amorphous and this drew attention to the effect of crystal structure on the polymerization mechanism. Adler *et al.*⁸⁻⁹ showed that the ESR spectrum of the irradiated radical was consistent with the crystal structure below -125°C and changed above -125°C to a spectrum characteristic to a dimer radical spectrum. The ESR spectrum at and above -20°C was similar to that of the polymer. These observations cast doubt on the usefulness of x-ray intensity data collected above -125°C .

Isakov¹⁹ reported on the crystal structure of acrylamide at -100°C . The space group was $P2_1/c$ with unit cell parameters of $a=840.8(3)$ pm, $b=579.2(3)$ and $\beta=118^{\circ}34'(2)$. The R factor were 21% for the hol and 19.7% for the hk0 reflections.

In this study, the crystal structure of acrylamide determined at -150°C and single crystal of the compound was irradiated at different temperatures to observe the radiation damage that may take place in the crystal structure. From the results obtained a mechanism of solid-state polymerization of acrylamide induced by radiation will be proposed.

Experimental

Acrylamide obtained from American Cyanamide Corporation was recrystallized twice from chloroform, and once from acetone. The observed melting point was $83.8\pm 0.3^{\circ}\text{C}$. Single crystals of acrylamide were grown by slow evaporation from solution in acetone. The crystals were platelets with a measured thickness of about 0.25 mm. A crystal of $0.35 \times 1.80 \times 0.25$ mm was cut from the crystal platelet and placed in a glass capillary tube that was then sealed at both ends. The dimensions of crystal were measured from the magnified photographs taken on a polarizing microscope. The long axis was the b-axis, which showed parallel extinction between crossed polarizers.

Preliminary diffraction photographs at -150°C were taken using a precision camera with $\text{MoK}\alpha$ radiation (Zr filter; 35 kV and 15 mA). These were used to determine the approximate cell parameters and space group. Intensity data were collected and precise cell parameters were determined using a General Electric Single Crystal Orientar with a scintillation counter detector and pulse height discriminator. $\text{CuK}\alpha$ radiation (Ni filter, at 35 kV and 15 mA) was used.

The intensity data at -150°C were collected by the θ - 2θ scanning method. Background measurements, with stationary crystal and counter, on both sides of the reflection peak were taken by 10 seconds counting. For every unique reflection, the related reflection (180° in Θ away) was also measured. The total number of reflections measured between the 2θ angular limits of 10° to 130° were 670. Fifty reflections that were present at the 2θ angular limits studied were unobserved (zero intensity) reflections.

Results and Discussion

Crystal Structure of Acrylamide

The unit cell parameters of acrylamide were determined at three temperatures of -150°C , -100°C and -50°C . The cell parameters were refined for 24 reflections over wide 2θ angle range. The results are tabulated in Table 1. The change in the β angle with temperature is approximately linear. However, the change of cell dimensions deviate significantly from a linear variation with temperature. The cell parameters obtained at -100°C are considerably different from the values reported by Isakov¹⁹ at the same temperature. It indicates the presence of crystal damage at that temperature, because Isakov determined the crystal structure at -100°C , at which the crystal has to be exposed to radiation for long time. However, in this work, the crystal was exposed to x-ray radiation for a minimum time at -100°C to scan reflections used for cell parameter determination.

The space group was determined from absent reflection to be $P2_1/c$. The calculated density for four molecules per unit cell is 1.165 g/cm^3 . Thus, the calculated density agrees well with the density of 1.125

g/cm³ measured at room temperature. When the correction is made for difference in temperature, the agreement is much better.

Table 1. Cell parameters of acrylamide with e.d.s's in parantheses

Tepperature/C°	a/pm	b/pm	c/pm	β /°	V/m ³ × 10 ³⁰
-150	828.0(2)	578.0(4)	974.9(2)	119.62(4)	405.6
-100	830.5(2)	575.1(6)	973.4(3)	119.28(7)	405.2
-45	833.5(4)	579.5(8)	977.7(4)	118.85(8)	413.6

The structure was solved using direct method for heavy atoms and difference fourier for hydrogens. The least-square refinement converged with R=0.075, and R_w=0.090 for anisotropic heavy atoms and isotropic hydrogens. The function minimized in the least-square refinement was $\sum w[F_o^2 - F_c^2]^2$, where $w=1/\sigma^2(F_o^2)$ with $\sigma^2(F_o^2)=\sigma^2_{count}(F_o^2)+(0.055F_o^2)^2$. σ^2_{count} is the standard deviation for statistical counting.

The final positional and thermal parameters are shown in Tables 2 and 3, respectively.

Table 2. Fractional coordinates of acrylamide with e.d.s'in parantheses at-150° C.

Atom	x	y	z
O	0.1508(2)	0.2354(2)	0.1312(2)
N	0.1078(3)	0.3667(3)	0.3929(2)
C ₁	0.1754(3)	0.2736(3)	0.0177(2)
C ₂	0.2820(3)	0.4770(4)	0.0128(3)
C ₃	0.3487(4)	0.6349(4)	0.1261(3)
H ₁	0.022(5)	0.487(6)	0.381(4)
H ₂	0.124(4)	0.329(6)	0.308(4)
H ₃	0.295(4)	0.014(5)	0.422(4)
H ₄	-0.338(4)	0.126(6)	0.276(4)
H ₅	-0.431(6)	0.270(7)	0.382(4)

Table 3. Thermal parameters of acrylamide with e.s.d's in parantheses (For H's isotropic)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O	0.0564(4)	0.0325(6)	0.0302(3)	-0.0092(3)	0.0306(3)	-0.0062(2)
N	0.0559(4)	0.0265(6)	0.0265(3)	0.0097(4)	0.0303(3)	0.0040(3)
C ₁	0.0350(4)	0.0205(6)	0.0264(3)	0.0021(3)	0.0189(3)	0.0015(3)
C ₂	0.0383(4)	0.0238(7)	0.0351(4)	-0.0019(4)	0.0176(3)	0.0055(3)
C ₃	0.0507(5)	0.0.261(8)	0.0522(5)	-0.0019(5)	0.0189(4)	0.0010(3)
H ₁	2.4(6)					
H ₂	1.6(6)					
H ₃	1.2(5)					
H ₄	1.9(6)					
H ₅	3.3(8)					

The thermal parameters are very small because of low temperature (-150° C) structure determination. Oxygen has the highest temperature factors in the [100] and [001] directions. At the same time, H₁, which hydrogen bonds with oxygen also has a high temperature factor. This suggests that there is more vibration

in the dimer connections. As would be expected, C₃ terminal carbon shows the highest temperature factors among carbons. The thermal parameters suggest that the molecule vibrates as a rigid body assuming C₁ as center. This can be seen better from Fig.1, which is the stereoscopic view of the molecule with thermal ellipsoids drawn to enclose 50% probability. It also suggest that the two molecules forming dimer (Fig.2) will vibrate in such a way as to weaken the hydrogen bonding. The labeling of atoms and some nonbonded distances are also shown in Fig.2. The dimer has a planar structure.

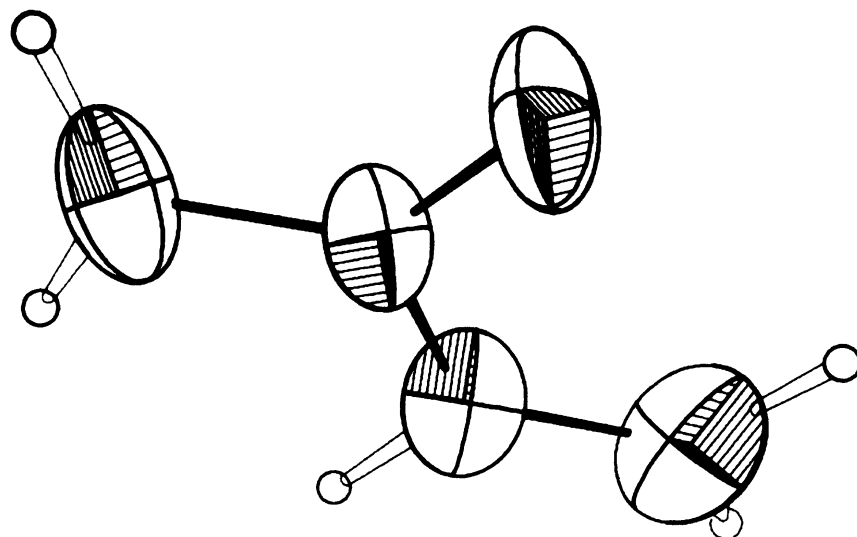


Figure 1. The molecule of acrylamide draw to eclose 50 % probability vibrations

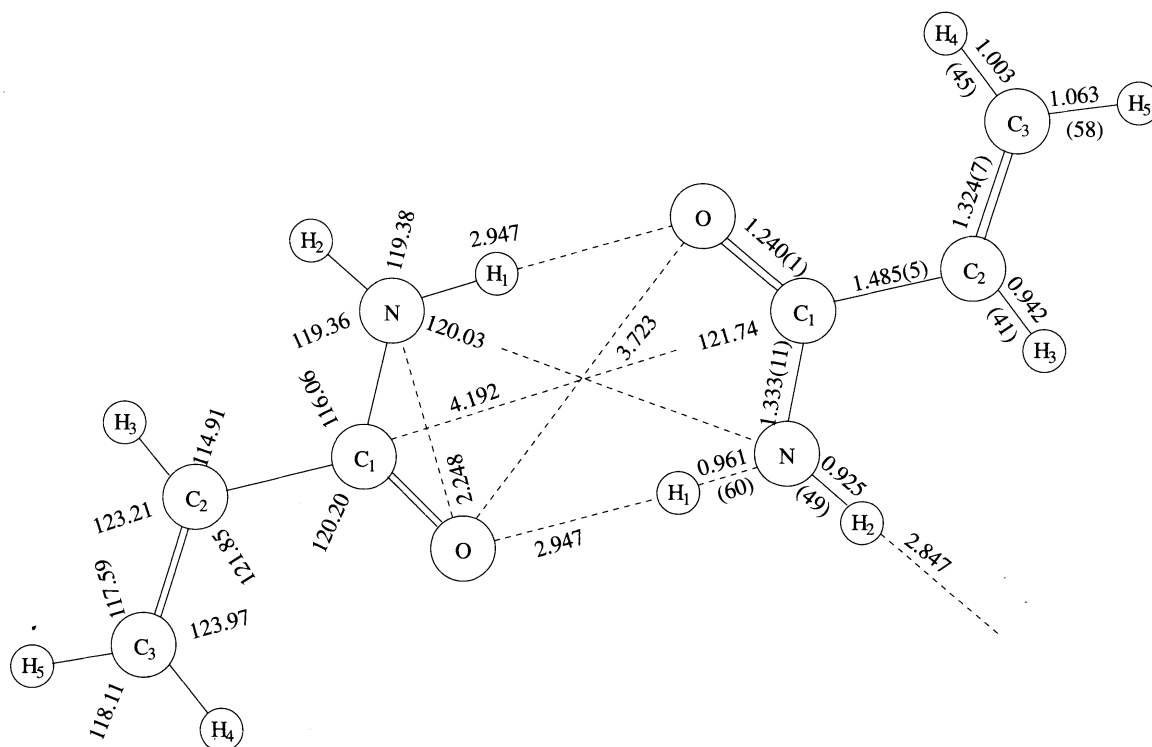


Figure 2. The dimer structure of acrylamide molecules with bond angles ad lengths (in Å).

The stereoscopic packing diagram of the unit cell of acrylamide is shown in Fig. 3. Unit cell contains four molecules oriented such a way that they can form dimer with molecules in other unit cell, but not within

the same unit cell. The molecules form layers parallel to the [001] direction with an interplanar distance of about 370 pm. In this arrangement the distance of $N-H_1 \cdots O$ in the dimer is 294.7 pm. Another hydrogen bond connects the dimer to another one with a distance for $N-H_2 \cdots O$ as 284.7 pm. The center of the dimer is also the center of the symmetry.

The bond lengths and bond angles of molecule are give in Table 4. The shorter bond distances of C_1-C_2 and $C=O$ and longer C_1-N than usual values are indicating the resonance structure of molecule. This is also observed from the deviation of bond angles from 120° of planar sp^2 hybridization. The relatively large standard deviation in positional and thermal parameters of the H atoms are expected result of radiation damage.

Radiation Damage of Acrylamide Structure

When acrylamide is irradiated with x-ray ions, radical ions and free radicals are generated. These species will react further at proper temperatures to give dimer, polymer, etc. In order to observe the changes at different temperatures, an acrylamide single crystal was cooled to $-150^\circ C$ and exposed to an x-ray beam. The x-ray intensities of several reflections that were measured, first increased then remained stable after 2-3 h of x-ray exposure. The increase of intensities for several reflections are shown in Table 5. Initially the mosaic blocks in single crystals are more nearly parallel and have fewer planes in the reflecting position at a given time. After thermal and radiation shock, mosaic blocks became slightly misaligned causing more planes to be in reflecting position. These effects have been use to decrease the extinction ²⁰ in the x-ray crystal structure determination.

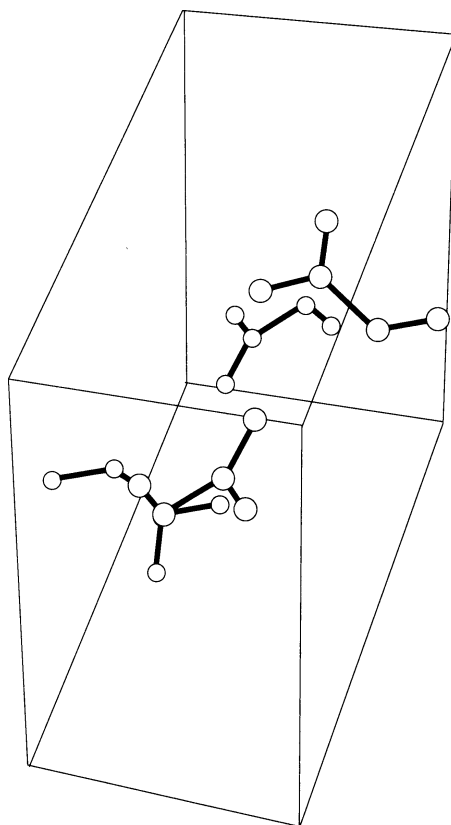


Figure 3. The stereoscopic packing diagram of a unit cell of acrylamide.

Table 4. Bond distances (pm) with e.s.d.'s in parentheses and bond angles ($^{\circ}$) (e.s.d.'s 0.1-0.2 $^{\circ}$ for nonhydrogen and 1.0-2.3 $^{\circ}$ for H atoms for acrylamide

C ₁ -O	124.0(1)	O-C ₁ -N	121.7
C ₁ -N	133.3(11)	O-C ₁ -C ₂	122.2
C ₁ -C ₂	148.5(5)	N-C ₁ -C ₂	116.1
C ₂ -C ₃	132.4(7)	C ₁ -C ₂ -C ₃	121.9
N-H ₁	96(6)	H ₁ -N-H ₂	119.4
N-H ₂	93(5)	H ₁ -N-C ₁	120.0
C ₂ -H ₃	94(4)	H ₂ -N-C ₁	119.4
C ₃ -H ₄	100(5)	C ₁ -C ₂ -H ₃	114.9
C ₃ -H ₅	106(6)	C ₃ -C ₂ -H ₃	123.2
		C ₂ -C ₃ -H ₄	124.0
		C ₂ -C ₃ -H ₅	117.6
		H ₄ -C ₃ -H ₅	118.1

Table 5. Change in intensities or reflectpons after 2-3 h of exposer to x-rays

hkl	Counts/10s	Count/10 s after intensity increase
100	26214	87522
200	40897	55998
300	7619	8150
400	8147	8538
500	706	729
600	721	737
700	132	131
002	49236	92791
008	1078	1126
020	24173	38099
040	498	510

After the intensities were stabilized at -150°C , the temperature was increased by about 5°C and the crystal was kept at that temperature for about one day without exposure to the x-rays, before cooling back to -150°C . The intensities of the same reflections were measured again at -150°C . The procedure was repeated, each time raising the temperature 5°C further up to about -10°C . There were no intensity changes for any reflections in the ranges of -150°C to -125°C . However, up to -50°C , the total decrease for a 020 reflection was about 20 % in 360 h. The greatest decrease in the intensities of 0k0 reflections occurred between -50°C and -20°C . At this time, the decrease in intensities of h00 and 001 reflections were almost zero. At about -20°C , the decreases were notable for all of the reflections observed. The crystal became turbid at -20°C indicating the presence of the polymer phase. The percent intensity decreased with respect to cumulative time of keeping crystal at -20°C (first at -50°C up to 360 h) for several reflections are shown in Fig.4.

Polymerization of acrylamide proceeds by a two phase mechanism^{8,18}. After the polymer phase separation, the unpolymerized monomer retains its crystal structure¹⁸. The 2θ -scan of h00 and 001 reflections for the undamaged crystal and about 90% polymerized crystal taken at -150°C are shown in Fig. 5. The weak reflections and the ones with a 2θ higher than about 40° are not observed after polymerization. However, the observed reflection peaks are quite sharp with small background. This is due to the phase separation of polymer during polymerization.

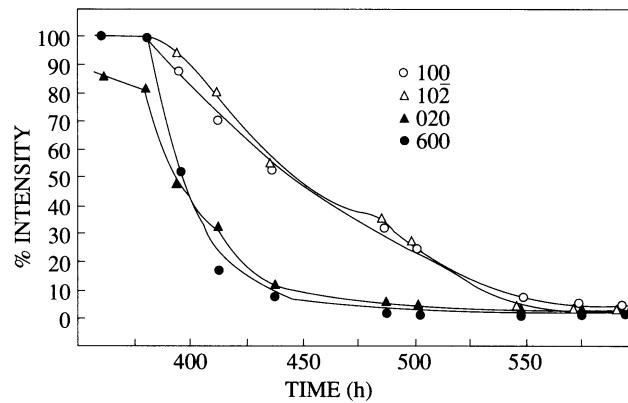


Figure 4 Percent x-ray intensity decrease of several reflections at -20°C with time for acrlamide.

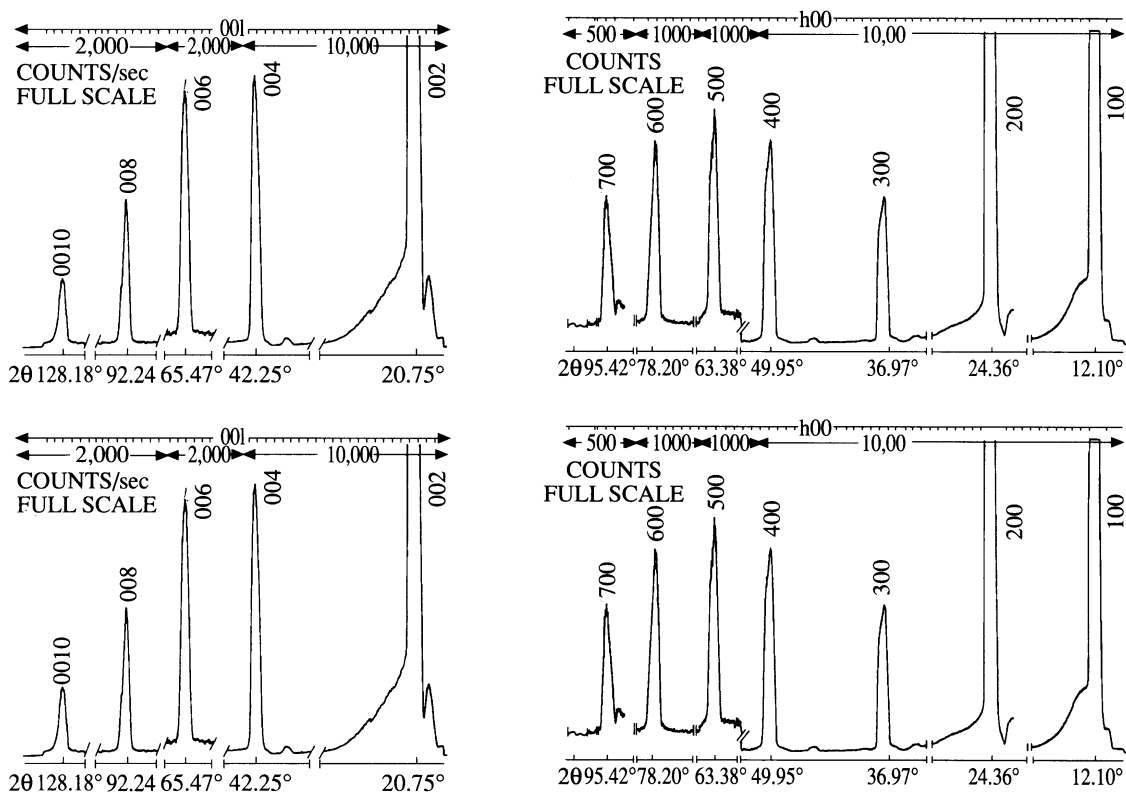
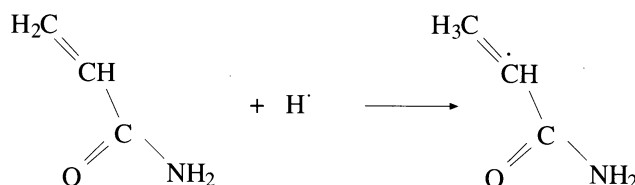


Figure 5. The x-ray spectrum of h00 and 001 reflections for acrlamide single crystal

Thus, the radiation damage in many organic crystals are significant and proper consideration should be given while determining the x-ray crystal structure of the radiation sensitive compounds.

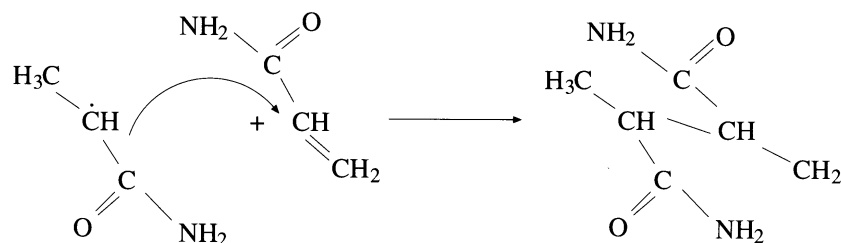
Mechanism of Radiation Induced Polymerization of Acrylamide in Solid-State

Initiation of the polymerization reaction proceeds by a series of steps; absorption of radiation energy, leading to excitation and ionization; liberation of a H atom which migrates and adds to an acrylamide monomer giving a radical; at a specified temperature (-125°C for acrylamide) or above this reacts with one monomer along a crystallographic axis, resulting in a contracted dimer radical trapped in an oriented direction within the crystalline matrix. Considerable strain energy is involved. Only at higher temperatures (-20°C or above for acrylamide) with more mobility and preferably at a crystal defect can this radical react with further monomer. The formation of active radical in acrylamide will be as follows:



In order to find which molecules in the unit cell can combine to give the dimer radical, non-bonding atomic distances (van der Waals contacts) within the limiting distance of about 430 pm or less should be investigated. The tail-to-tail combination of radical addition was ruled out, because Adler and Baysal⁸ showed from ESR results that radicals of the type $\text{CH}_3 \cdot \text{CHCONH}_2$ were involved in the dimerization. Thus if the head-to-tail combination of C_2 to C_3 is considered, there are two C_3 atoms (C'_3 and C''_3 in other unit cells) at suitable combination distances of 396.3 pm and 387.1 pm. Molecules containing C_2 and C'_3 are related to each other along the screw axis, while molecules of C_2 and C''_3 are not. Data on the relative rate of the decrease in the intensities of the different reflections (Fig. 4) showed that the attack of the primary radical to the monomer to form the dimer radical takes place along the screw-axis. Therefore, only C'_3 can combine with C_2 by head-to-tail combination. In this case, one of the molecules has to flop over to be able to combine with another molecule. This would cause the dimer radical to assume a different orientation from the parent crystal lattice. However, it was reported⁸ from ESR results that the dimer radical is oriented with respect to the crystal lattice. Therefore, head-to-tail addition of this type is also not possible.

If the reaction is of the head-to-head type, then C_2 of reference molecule has to combine with C_2 in other molecules. There is only one C'_2 of that type in the proper combination distance (375.0 pm). In this case the molecules do not have to flop over to produce a dimer radical which is also oriented with respect to crystal lattice. The reaction will be as follows:



After formation of the dimer radical, the C_2 — C'_2 distance will change from 375.0 pm to 154 pm. This will cause a contraction in the screw-axis direction. The distance between C'_2 and another C''_2 or C''_3 along the screw-axis is much larger than the van der Waals contact and therefore, the third molecule added to dimer radical can hardly be along the screw-axis direction. Thus, the preferential orientation of the growing chain is lost on further polymerization. The polymer is amorphous, and polymerization takes place at the polymer-monomer interface. The phase separation of monomer and polymer can be seen distinctly even with naked eye on the single crystal of monomer.

Acknowledgments

The author wishes to thank Prof. Dr. Bahattin Baysal for bringing this subject to his attention, and Dr. George Adler for his valuable contributions in every stage of this work.

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