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Conformational Effects on the Cyclopolymerization of *N*-(*p*-Bromophenyl)dimethacrylamide

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ABSTRACT: *N*-(*p*-Bromophenyl)dimethacrylamide was synthesized and polymerized in the solid state by irradiation with cobalt-60 γ rays. Analysis of the polymer indicated that the monomer cyclized completely and that both five- and six-membered rings were formed. The orientation of the double bonds in the crystal lattice was determined by single-crystal X-ray diffraction. In all cases the distances separating two potential intramolecular reactors were appreciably less than those separating the potential intermolecular reactors. It was concluded that the monomer crystallized in a conformation that would favor the intramolecular over the intermolecular polymerization reaction. The percentages of five- and six-membered rings could not be predicted from the crystallographically determined atomic positions. Electron spin resonance measurements on the polycrystalline sample indicated that the radical centers generated by the irradiation were stable for long periods. Radical-initiated solution polymerization of the monomer produced a cyclopolymer containing predominantly the less stable ring size, the five-membered ring, when the reaction was performed at 58 °C. At 114 °C, however, the percentage of the thermodynamically favored six-membered ring was increased. Changes in the polarity of the solvent had little effect on the structure of the polymer. The appearance of a new imide stretching band in the infrared spectrum of the monomer could be indicative of conformational changes upon dissolution.

Introduction

Since the original mechanistic proposals,[1,2] cyclopolymerization of nonconjugated dienes has become a widely accepted and thoroughly researched polymerization phenomenon. The formation of cyclic units along the polymer backbone is generally believed to occur through an alternating intramolecular–intermolecular propagation reaction.[1,2]

No one totally satisfactory mechanism exists at present that can adequately account for all the experimental observations. Butler[3] postulated that there may exist a through-space, electronic interaction between the double bonds of the diene, which should provide a more energetically favored reaction pathway by cyclization rather than by linear propagation involving only one double bond per molecule. On the other hand, Gibbs and Barton[4] proposed that steric factors alone control the course of the reaction. After initiation of the first double bond, the second double bond would frequently be presented to the reaction site in a conformation favorable for reaction and would, at the same time, sterically shield the reaction site from other monomers. Once formed, the cyclized radical would be much less sterically hindered and could participate in an intermolecular propagation reaction. There exists experimental evidence which supports each of the proposals,[5–15] and this problem is still very much a center of active research in the area.

Butler and Myers[13,15] reported an investigation into the spectroscopic and polymerization characteristics of a series of N-substituted dimethacrylamides. They attempted to find bathochromic shifts in the ultraviolet (UV) spectra and changes in the chemical shifts of the relevant protons in these dienes that would provide evidence for a "prealigned" conformation favoring the cyclization propagation step. They also argued that if such an interaction did exist between the nonconjugated double bonds, it might persist in the solid state. Irradiation with ionizing cobalt-60 γ rays would then be expected to lead to the formation of a highly cyclized polymer with a high degree of regularity in the repeating unit.

However, the monomer spectra were much more complicated than expected, with the interaction of the nitrogen through the carbonyls affecting most of the observed transitions. Chemical shifts in the vinyl protons from the proton magnetic resonance (^{1}H NMR spectra varied as the nitrogen substituent was changed from hydrogen to methyl to phenyl. It was proposed that these observed shifts would be consistent with a cis–trans orientation of the imide group and an s-trans orientation of the methacryl group.

Solid-state polymerization produced a linear polymer that was highly cyclized. Contrary to free radical initiation, which produced polymers composed nearly exclusively of five-membered rings, the solid-state polymers had a more random distribution of ring sizes—there was an appreciable proportion of both five- and six-membered rings. Therefore, even though the monomer appeared to be preoriented in a manner that highly favored the cyclization step, it was concluded that the crystal lattice must not control the direction of the cyclization step.

The earlier work[13,15] served to pose yet another question—that concerning the actual processes occurring in the solid-state polymerization of the dimethacrylamides. Does the crystal actually control the course of the reaction, and is the monomer actually preoriented in a conformation favoring cyclization? Is the presence of both five- and six-membered rings indicative of random processes occurring in the crystal, or would they be expected if a greater knowledge of the monomer conformation were available? How much, if at all, can these processes be extrapolated to the solution processes?

In an attempt to answer these questions, *N*-(*p*-bromophenyl)methacrylamide was chosen for an extensive study of its structure and polymerization behavior in both the solid and solution states. Para substitution by bromine aided in determination of the monomer structure by uti-

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lization of heavy-atom techniques in an X-ray diffraction investigation.

Experimental Section

Materials and Equipment. A description is available as supplementary material.[23]

Monomer Synthesis. *N*-(*p*-Bromophenyl)methacrylamide. This compound was prepared by the previously reported[15] method for *N*-phenylmethacrylamide, with slight modifications: yield 72.2 g (62%); mp 117–118 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3), 5.45 (s, 1), 5.80 (s, 1), 7.45 (m, 5); IR (Nujol) 3315 (m), 1670 (m), 1615 (ms), 1590 (m), 1500 (s), 930 (s), 820 (s) cm^{-1}.

***N*-(*p*-Bromophenyl)dimethacrylamide.** The monomer was synthesized by the previously reported method for *N*-phenyldimethacrylamide, with slight modifications: yield 11.53 g (37.6%); mp 105–106.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 6), 5.55 (m, 4), 7.25 (m, sh, 4); IR (KBr) 3000 (w), 1705 (s), 1690 (s), 1620 (m), 1490 (m), 1450 (m), 1315 (s), 1165 (s), 820 (s), 500 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{14}BrNO_2$: C, 54.56; N, 4.54; H, 4.57; Br, 25.92. Found: C, 54.70; N, 4.49; H, 4.50; Br, 26.08.

Solid-State Polymerization. Calibration of the cobalt-60 source was performed for each irradiation position by Fricke dosimetry.[16] The dosimetry and subsequent monomer irradiations were performed in 10-mm Pyrex tubes. The design and construction of the irradiator have been previously described in the literature.[17]

The irradiations were performed primarily as previously described.[13] Crystalline *N*-(*p*-bromophenyl)dimethacrylamide was placed in a 10-mm Pyrex tube, evacuated to 10^{-5} mm, and sealed. The tube was then placed in an appropriate sample holder adjacent to the source and irradiated for a predetermined period. Irradiations were performed at liquid nitrogen and ambient temperatures. The sample was kept in the dark at room temperature to allow time for postpolymerization. At the end of that period, the crystals were dissolved in 25 mL of acetone, and the resulting solution was dripped slowly into 400 mL of rapidly stirring hexane. Precipitated polymer was collected by suction filtration, and the precipitation process was repeated. The product was dried in vacuo for 24 h, and the yield was determined.

When polymerization was attempted with a total dose of 2 Mrd at −196 °C and a 30-day postpolymerization period, no polymer was obtained, and the ^{1}H NMR of the irradiated compound indicated essentially no changes had occurred in the monomer recovered (~98%). Similarly, little change was observed in the crystals when the total irradiation was 60 Mrd at ambient temperature with a 6-day postpolymerization period. However, when the total dose was increased to 130 Mrd and the irradiation was carried out at ambient temperature with a 6-day postpolymerization, the monomer crystals turned slightly beige but were still readily soluble in acetone. Precipitation in the nonsolvent and subsequent treatment as described above yielded 0.161 g (16.1% conversion) of a fine, white static powder, softening point 185–193 °C.

Solution Polymerization. Free Radical Initiation. Before use, all glassware was cleaned, rinsed with acetone, and dried in a 100 °C oven overnight. In a typical experiment, 15 mL of a 0.5 M solution of *N*-(*p*-bromophenyl)dimethacrylamide (in benzene or DMF) containing 1% recrystallized azobis(isobutyronitrile) was placed in a heavy-walled Pyrex polymerization tube. The tube was then connected to a high-vacuum line and, through a series of freeze–thaw cycles, was evacuated to 10^{-5} mm and sealed. The tube was then placed in an oil bath maintained at a constant temperature for the specified time. The tube was opened at the end of the reaction period, and the polymer was precipitated by dripping slowly into a rapidly stirred 1:1 mixture of hexane and diethyl ether. The polymer was collected by suction filtration through a sintered glass funnel and dried to a constant weight in a 60 °C oven. To obtain samples for spectral studies, the polymer was dissolved, and reprecipitated, and dried to a constant weight.

X-ray Diffraction Study. Suitable crystals for the diffraction study were grown by slow evaporation from a diethyl ether solution. Preliminary Weissenberg rotation photographs indicated that the crystal symmetry was orthorhombic *mmm*. Indexing of the reflections eliminated all space groups but *Pbca* and *Pcca*. Zero-, first-, and second-level precession photographs were then made, and observation of the systematic absences determined the most probable space group to be *Pbca*.

Table I
Crystal Data for *N*-(*p*-Bromophenyl)dimethacrylamide

parameter	data
symmetry	orthorhombic
space group	*Pbca*
color	colorless
crystal dimensions, mm	0.028 × 0.134 × 0.103
measured[18] density, g/cm^3	1.492
calcd density, g/cm^3	1.489
Z (no. of molecules/ unit cell)	8
formula	$C_{14}H_{14}BrNO_2$
mol wt	308.20
2θ(max), deg	115.0
no. of obsd reflections	1162
no. of unobsd reflections	707
cell dimensions	
$\alpha = \beta = \gamma$, deg	90.0
a, Å	29.727
b, Å	8.561
c, Å	10.792
volume, Å^3	2746.49

Table II
Structure Refinement of *N*-(*p*-Bromophenyl)dimethacrylamide

parameter	data
initial *R*	0.26
no. of cycles of FMLSQ isotropic thermal parameters H's not included	3
R after FMLSQ	0.17
no. of cycles of BDLSQ anisotropic thermal parameters H's not included	6
R after BDLSQ	0.077
no. of cycles of BDLSQ anisotropic thermal parameters H's included, but not refined	3
R after BDLSQ	0.068
no. of cycles of BDLSQ anisotropic thermal parameters H's included and refined	9
final *R*	0.058

Each photograph was examined for possible evidence of polymerization occurring under the influence of the X-ray irradiation during geometric data collection. The diffuse rings expected if polymer had been forming did not appear.

A new crystal was centered on a Syntex P$\bar{1}$ diffractometer and, after centering 15 intense reflections, accurate cell constants were determined. Pertinent crystal data are summarized in Table I. The intensity data were collected at ambient temperature using copper Kα radiation (λ = 1.5418 Å). The details are similar to those given by Dymock and Palenik.[19] Four standard reflections were measured at 100-reflection intervals and were used to correct for any variation of intensities with time.

Scattering factors for bromine, oxygen, nitrogen, and carbon were obtained from ref 20, while those of hydrogen were obtained from Stewart, Davidson, and Simpson.[21] The values for bromine were corrected for anomalous dispersion of the copper Kα irradiation.

A Patterson function[22] was calculated to determine the approximate positional coordinates of bromine. The positions of the other nonhydrogen atoms were located by using Fourier syntheses[22] iteratively. An overall scale factor was calculated, and the model structure was refined by a least-squares minimization.[22] After refinement using first isotropic and then anisotropic thermal parameters, a difference Fourier synthesis was calculated, and the hydrogen atoms were located. These positions were included in the subsequent least-squares calculations. The reliability index, *R*, was calculated, where $R = \sum |F_o - F_c| / \sum F_o$. The shifts were small, so the refinement was terminated. An outline of the scheme

Table III
Final Positional Parameters and Their Estimated Standard Deviations for *N*-(*p*-Bromophenyl)dimethacrylamide

atom[a]	x	y	z
C9′	3752 (3)	7028 (10)	4906 (9)
C8′	3452 (3)	6577 (10)	5724 (8)
C7′	3316 (3)	4874 (10)	5784 (8)
O′	2936 (2)	4492 (7)	6017 (5)
N	3658 (2)	3756 (7)	5506 (6)
C7	3522 (2)	2317 (11)	4995 (8)
O	3727 (2)	1126 (6)	5258 (6)
C8	3155 (2)	2362 (11)	4069 (8)
C9	3162 (3)	3432 (12)	3180 (9)
Me′	3168 (4)	7642 (13)	6548 (10)
Me	2825 (3)	1112 (12)	4168 (10)
C4	4084 (2)	3892 (9)	6129 (8)
C3	4473 (3)	3480 (10)	5477 (8)
C2	4886 (2)	3590 (10)	6070 (9)
C1	4910 (2)	4111 (10)	7272 (8)
C6	4522 (2)	4553 (10)	7927 (8)
C5	4107 (2)	4422 (11)	7334 (7)
Br	5471 (0)	4334 (2)	8067 (1)

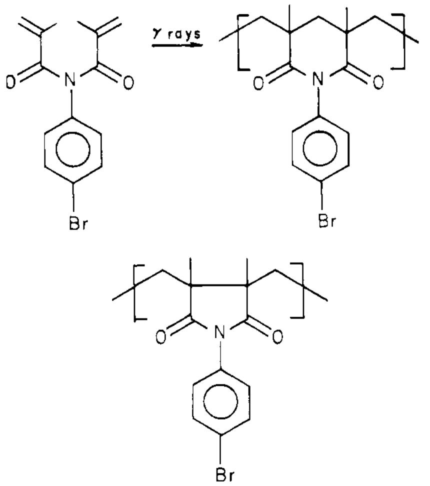
[a] Values for all atoms times 10^4.

of structure refinement is given in Table II. The final positional and thermal parameters for the nonhydrogen atoms are given in Tables III and IV; the positional and thermal parameters for the hydrogen atoms are given in Table V. Bond distances and angles are listed in Tables VI and VII, respectively. Selected dihedral angles are given in Table VIII. Tables of observed and calculated structure factors are available as supplementary material.[23]

Electron Spin Resonance (ESR). Sample cells, similar to those described by Adler, Ballantine, and Baysal,[24] were used for the irradiation of the monomer. The narrow portion of the cell was made of Amersil quartz, however, and was joined to the Pyrex portion by a graded seal. The crystalline monomer was placed in the wide end of the tube. After irradiation, the quartz tube was annealed with a blow torch to remove the color centers created by the γ rays. The sample was simultaneously kept cold by immersion of the wide end in liquid nitrogen. The sample was then shaken into the annealed portion of the tube, and the ESR spectra were recorded at room temperature over a time span of 1 month. The tube was then opened to the atmosphere, and the spectra were recorded over a period of several days to measure the effect of oxygen on the spectra.

Results

Solid-State Investigation. Structure of the Solid-State Polymer. Solid-state initiation by cobalt-60 γ rays resulted in the formation of isolable polymer only after high total doses at ambient temperature. After exposure to 130 Mrd, only 16% conversion of monomer to polymer was obtained. The resulting polymer was readily soluble in common organic solvents. Infrared (IR) analysis revealed no detectable absorptions for alkene–H stretching and bending vibrations. Similarly, no vinyl absorptions were detected in the ^{1}H NMR spectrum of the polymer, indicating little or no residual unsaturation. It was therefore concluded that polymerization occurred with cyclization and that the polymer backbone could be composed of five- or six-membered rings or both as shown in eq 1.



(1)

To aid in identifying the repeating unit(s), the sensitivity of carbonyl stretching frequencies to the ring size of imides was utilized. Examination of the 1600–1800-cm^{-1} range in the IR spectrum of poly[*N*-(*p*-bromophenyl)dimethacrylamide] revealed a strong absorption at 1710 cm^{-1} and shoulders at approximately 1780, 1730, and 1680 cm^{-1}. Comparison with IR spectra reported by Sokolova and Rudkovskaya[25] indicated that the former two absorptions correlated well with the carbonyl stretch of six-membered cyclic imides [*N*-phenylglutarimide and the polymer resulting from the deamination of poly(*N*-phenylmethacrylamide)]. The latter two absorptions were nearly identical with those reported for the five-membered cyclic imide *N*-phenylsuccinimide. IR analysis therefore afforded strong evidence for the existence of both five- and six-membered rings in the solid-state polymer.

To increase the resolution and minimize the conformational broadening of the proton signals, the ^{1}H NMR

Table IV
Final Thermal Parameters and Their Estimated Standard Deviations for *N*-(*p*-Bromophenyl)dimethacrylamide

atom[a]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C9′	13 (12)	117 (18)	98 (11)	−12 (8)	2 (6)	24 (25)
C8′	12 (12)	87 (14)	76 (10)	19 (7)	−18 (6)	−42 (23)
C7′	10 (1)	93 (15)	57 (9)	14 (7)	−8 (5)	1 (21)
O′	7 (1)	110 (10)	104 (7)	7 (5)	4 (3)	−3 (17)
N	8 (1)	58 (10)	72 (7)	−6 (5)	−1 (4)	−33 (16)
C7	9 (1)	93 (14)	69 (8)	−14 (7)	12 (5)	−33 (23)
O	12 (1)	61 (8)	132 (8)	−1 (5)	−8 (4)	−20 (15)
C8	8 (1)	104 (14)	72 (9)	−3 (8)	1 (5)	−72 (24)
C9	14 (1)	177 (19)	71 (10)	−7 (8)	−13 (7)	23 (27)
Me′	26 (2)	86 (16)	135 (14)	−8 (11)	10 (9)	−50 (28)
Me	15 (1)	144 (19)	154 (15)	−39 (9)	−37 (8)	−2 (31)
C4	7 (1)	63 (13)	71 (9)	−4 (6)	−6 (5)	6 (19)
C3	8 (1)	107 (14)	68 (9)	0 (7)	2 (5)	−7 (21)
C2	7 (1)	107 (15)	98 (11)	−8 (7)	7 (6)	2 (24)
C1	8 (1)	92 (16)	106 (12)	−11 (7)	−17 (5)	36 (23)
C6	8 (1)	134 (15)	77 (8)	8 (8)	−10 (6)	7 (24)
C5	8 (1)	123 (15)	66 (9)	0 (8)	8 (4)	13 (23)
Br	9 (0)	302 (2)	148 (1)	6 (1)	−28 (1)	−59 (4)

[a] Values for all atoms times 10^4.

Table V
Final Positional and Isotropic Thermal Parameters and Estimated Standard Deviations for Hydrogen Atoms of *N*-(*p*-Bromophenyl)dimethacrylamide

atom 1	bonded to atom 2	x^a	y^a	z^a	β, Å^2
H2	C2	5145 (26)	3376 (98)	5634 (74)	5.8 (2.3)
H3	C3	4426 (18)	3341 (69)	4630 (54)	1.6 (1.4)
H5	C5	3842 (18)	4606 (72)	7769 (54)	1.6 (1.4)
H6	C6	4532 (23)	5041 (81)	8903 (66)	3.9 (1.8)
H91	C9	2900 (21)	3391 (76)	2556 (64)	3.2 (1.7)
H92	C9	3418 (23)	3802 (87)	3096 (74)	4.7 (2.0)
H93	C9′	3859 (23)	7921 (89)	4710 (71)	4.8 (2.1)
H94	C9′	3911 (30)	6344 (108)	4074 (87)	8.1 (2.8)
HM1	Me	2704 (30)	685 (123)	3526 (90)	10.0 (3.0)
HM2	Me	2579 (39)	1310 (132)	3570 (103)	12.1 (3.8)
HM3	Me	2918 (22)	421 (92)	4144 (67)	4.0 (1.9)
HM4	Me′	3038 (35)	7144 (151)	7516 (112)	14.3 (3.7)
HM5	Me′	3292 (24)	8233 (88)	6540 (70)	3.8 (2.1)
HM6	Me′	3362 (33)	7488 (154)	7261 (104)	12.7 (3.3)

[a] Values for all positional parameters times 10^4.

Table VI
Bond Distances (Å) with Their Estimated Standard Deviations for *N*-(*p*-Bromophenyl)dimethacrylamide

atoms	distance	atoms	distance
Br-C1	1.883 (8)	C2-H2	0.919 (79)
C1-C2	1.374 (13)	C3-H3	0.932 (58)
C2-C3	1.388 (11)	C5-H5	0.931 (55)
C3-C4	1.400 (11)	C6-H6	1.133 (71)
C4-C5	1.380 (12)	C9-H91	1.030 (66)
C5-C6	1.393 (11)	C9-H92	0.830 (71)
C6-C1	1.407 (11)	Me-HM1	0.862 (98)
C4-N	1.439 (10)	Me-HM2	0.990 (114)
N-C7	1.409 (11)	Me-HM3	0.653 (77)
C7-O	1.222 (10)	C9′-H93	0.856 (76)
C7-C8	1.479 (11)	C9′-H94	1.172 (93)
C8-C9	1.327 (13)	Me′-HM4	1.193 (121)
C8-Me	1.456 (13)	Me′-HM5	0.624 (75)
N-C7′	1.428 (10)	Me′-HM6	0.970 (108)
C7′-O′	1.203 (9)		
C7′-C8′	1.514 (12)		
C8′-C9′	1.312 (13)		
C8′-Me′	1.527 (14)		

Table VII
Bond Angles (Deg) with Their Estimated Standard Deviations for *N*-(*p*-Bromophenyl)dimethacrylamide

atoms	angle	atoms	angle
Br-C1-C2	120.6 (0.6)	Me′-C8′-C9′	126.2 (0.8)
C1-C2-C3	120.2 (0.8)	C1-C2-H2	120.3 (5.1)
C2-C3-C4	118.9 (0.8)	H2-C2-C3	119.3 (5.1)
C3-C4-C5	121.0 (0.7)	C2-C3-H3	126.4 (3.6)
C4-C5-C6	120.3 (0.8)	H3-C3-C4	113.6 (3.6)
C5-C6-C1	118.3 (0.8)	C4-C5-H5	119.3 (3.6)
C6-C1-C2	121.3 (0.8)	H5-C5-C6	120.2 (3.6)
Br-C1-C6	118.1 (0.6)	C5-C6-H6	118.8 (3.6)
C3-C4-N	118.3 (0.7)	H6-C6-C1	122.9 (3.6)
C5-C4-N	120.8 (0.7)	C8-C9-H91	115.9 (3.8)
C4-N-C7	120.4 (0.6)	H91-C9-H92	129.5 (6.4)
C7-N-C7′	118.3 (0.6)	C8-C9-H92	110.9 (5.2)
C4-N-C7′	117.6 (0.6)	C8-Me-HM1	122.2 (6.6)
N-C7-O	119.7 (0.7)	C8-Me-HM2	108.8 (6.6)
N-C7-C8	117.0 (0.7)	C8-Me-HM3	112.3 (6.5)
O-C7-C8	123.1 (0.8)	HM1-Me-HM2	40.6 (9.2)
C7-C8-C9	119.6 (0.8)	HM1-Me-HM3	76.0 (9.1)
C7-C8-Me	115.3 (0.8)	HM2-Me-HM3	116.1 (9.2)
Me-C8-C9	124.9 (0.8)	C8′-C9′-H93	133.1 (5.0)
N-C7′-O′	122.0 (0.7)	H93-C9′-H94	96.1 (6.7)
N-C7′-C8′	116.5 (0.7)	C8′-C9′-H94	130.0 (4.6)
O′-C7′-C8′	121.4 (0.7)	C8′-Me′-HM4	118.4 (5.8)
C7′-C8′-C9′	119.5 (0.8)	C8′-Me′-HM5	98.7 (6.9)
C7′-C8′-Me′	113.7 (0.8)	C8′-Me′-HM6	98.1 (6.8)
HM4-Me′-HM5	119.5 (9.0)		
HM4-Me′-HM6	56.6 (8.9)		
HM5-Me′-HM6	76.9 (9.6)		

Table VIII
Selected Dihedral Angles (Deg) for *N*-(*p*-Bromophenyl)dimethacrylamide

atoms	angle	atoms	angle
C9′-C8′-C7′-N	33.68	C7′-C8′-C9′-H93	1.69
C8′-C7′-N-C7	208.81	C7′-C8′-C9′-H94	181.03
C7′-N-C7-C8	39.58	C9′-C8′-Me′-HM4	43.94
N-C7-C8-C9	44.34	C9′-C8′-Me′-HM5	160.71
C9′-C8′-C7′-(Me′)	189.02	C9′-C8′-Me′-HM6	288.41
C9′-C8′-C7′-O′	215.93	C7-C8-C9-H91	1.85
C7′-N-C7-O	213.98	C7-C8-C9-H92	177.50
N-C7-C8-Me	220.30	C7-C8-Me-HM1	123.47
C8′-C7′-N-C4	50.24	C7-C8-Me-HM2	2.63
C7′-N-C4-C3	325.45	C7-C8-Me-HM3	245.86
N-C4-C3-C2	180.69	N-C4-C3-H3	347.64
C4-C3-C2-C1	0.68	C4-C3-C2-H2	185.11
C7′-N-C4-C5	145.87	N-C4-C5-H5	2.43
N-C4-C5-C6	179.80	C4-C5-C6-H6	168.92
C3-C2-C1-Br	177.63		

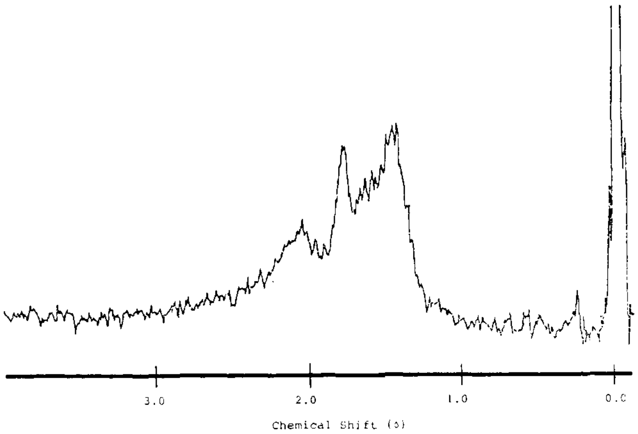


Figure 1. ^{1}H NMR spectrum (100 MHz) of the solid-state polymer of *N*-(*p*-bromophenyl)dimethacrylamide. The spectrum was run at 145 °C; solvent was nitrobenzene.

analysis of the polymer was performed at 100 MHz and at elevated temperature. The high-field region of the spectrum obtained is given in Figure 1. The resonances at δ 1.47 and 1.71 correspond to the chemical shifts reported for the methyl hydrogens on a five- and six-membered cyclic imide ring, respectively.[13] The two peaks are very broad, however, and overlap makes quantitative assessment of the structure approximate at best.

Determination of the Monomer Structure. One of the most unequivocal, practical methods of determining the solid-state conformation of a molecule, and the method of choice in this study, is X-ray diffraction analysis. A drawing illustrating the atomic numbering system used for *N*-(*p*-bromophenyl)dimethacrylamide is given in Figure 2. The computer-generated ORTEP drawing for the nonhydrogen atoms is given in Figure 3.

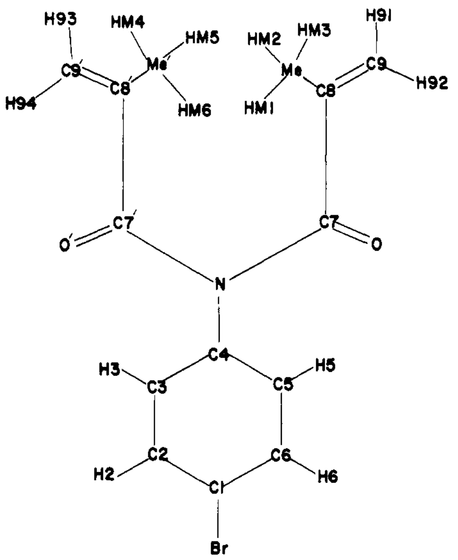


Figure 2. Numbering scheme used in the X-ray analysis of *N*-(*p*-bromophenyl)dimethacrylamide.

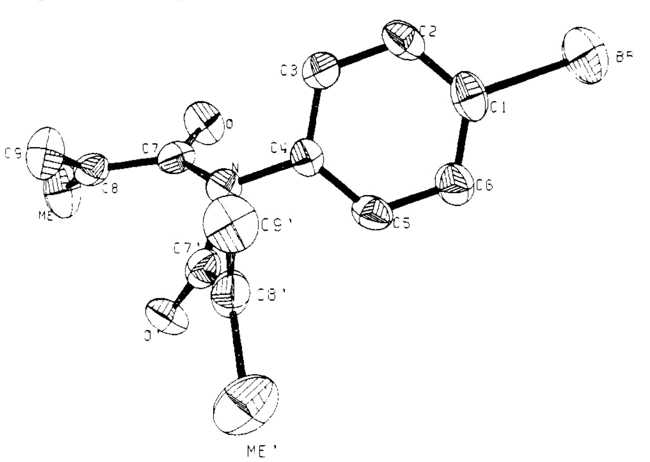
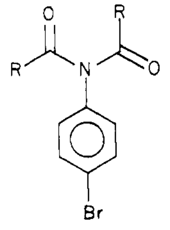


Figure 3. ORTEP drawing of *N*-(*p*-bromophenyl)dimethacrylamide showing the atomic numbering and thermal ellipsoids.

Examination of the ORTEP drawing led to several interesting observations. First, the imide group was roughly in a trans–cis orientation, as in 1. This correlated well with the early predictions[15] that dimethacrylamides would be conformationally similar to diacetamide and *N*-methyldiacetamide. However, the predicted coplanar arrangement of the imide group that would allow maximum delocalization of the π clouds was not observed. Dihedral angle measurements indicated that O′ was skewed out of the plane containing C7′–N–C7 by 26.6°, while O was skewed out by 34.18°. The phenyl ring oriented in a plane with a dihedral angle of 65° to the imide plane, and, therefore, extended conjugation of the imide group through the phenyl ring would also be unlikely.



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Equally striking, albeit somewhat expected, was the observation that neither of the methacryl groups had a coplanar arrangement of the carbon–carbon double bond and the carbonyl in the crystalline state. A dihedral angle of 215.9° between the atoms C9′–C8′–C7′–O′ was nearly 36° from that coplanar orientation. Similarly, the atoms O–C7–C8–C9 oriented with a dihedral angle of 230.16°, which was roughly 50° from a coplanar arrangement. Though both groups were in the s-trans orientation, the molecule had crystallized in a conformation that did not allow maximum overlap of the π clouds, presumably in a higher energy conformation.

Table IX
Pertinent Intramolecular and Intermolecular Distances (Å) for Atoms Involved in the Solid-State Polymerization of *N*-(*p*-Bromophenyl)dimethacrylamide

	intramolecular reactors		closest intermolecular reactor	
atom	atom	distance	atom	distance
C9	C8′	3.940	C8	4.489
	C9′	4.002		
C8	C8′	4.122	C9	4.489
	C9′	4.453		
C8′	C8	4.122	C9′	4.753
	C9	3.940		
C9′	C8	4.453	C8′	4.753
	C9	4.002		

Perhaps the most interesting aspect of the monomer conformation and certainly the most relevant to the polymerization process was the relative orientation of the two double bonds with respect to each other. The plane containing C9′–C8′–Me′ and that containing C9–C8–Me were at an angle of 87.45° to each other. This nearly perpendicular arrangement would almost certainly allow no possibility for the through-space overlap of those π clouds, and it was obvious that the monomer had not crystallized in a conformation that maintained the proposed[3] nonconjugated interaction of the double bonds.

If the high degree of cyclization obtained in the solid-state polymerization was not the result of a "preorientation" based on a nonconjugated interaction, why then did it occur? Such a question could not, of course, be answered with the data of a single isolated monomer in the crystal lattice. It was, therefore, necessary to examine the intermolecular as well as the intramolecular orientations of the reacting double bonds. The initial investigation centered on the packing of the molecule in the unit cell in the eight symmetry-related positions. The computer-generated packing diagram of a unit cell is reproduced in Figure 4. Orientations of the molecules in adjacent unit cells must also play a crucial role in the polymerization process. Considering a unit cell, the symmetry-related positions of monomers in cells directly above, below, and to either side of that unit cell were also plotted. From the positions of these atoms, the intramolecular and intermolecular distances separating the atoms involved in the polymerization process (C8, C9, C8′, C9′) were calculated. A brief summary of the most pertinent distances is given in Table IX. Intramolecular distances from C9 to C8′ and C9′ were 3.940 and 4.002 Å, respectively, while the closest intermolecular reactive site was nearly $^1/_2$ Å further away (4.489 Å to C8). The closest intramolecular route for C8 was with C8′, which was 4.122 Å away. The other intramolecular site, C9′, was 4.453 Å removed, which was almost as far away as the nearest intermolecular site (C9 at 4.489 Å). The atom C8′ was fairly close to its two possible intramolecular reactors, which were C8 at 4.122 Å and C9 at 3.940 Å. The closest intermolecular reactor, C9′, was 0.6 Å further away. Finally, the closest intramolecular reacting site for C9′ was C9, which was 4.002 Å away. The second intramolecular possibility, C8, was 0.4 Å further away, and the nearest potential intermolecular route was even further separated (C8′ at 4.753 Å). All of

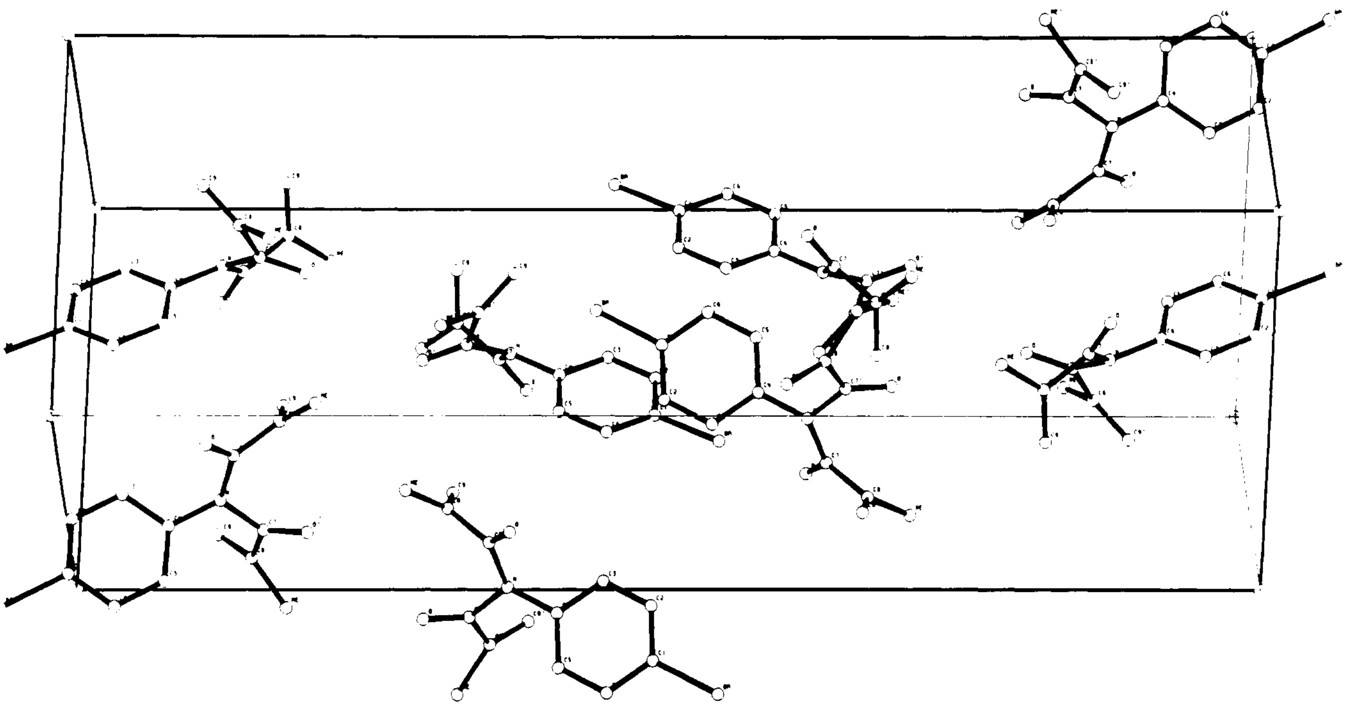
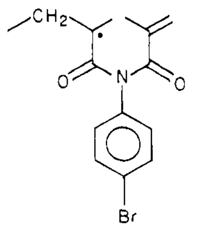


Figure 4. Packing diagram of the unit cell of *N*-(*p*-bromophenyl)dimethacrylamide showing the eight symmetry-related positions.

the carbons in the double bonds had at least one and, in some cases, two potential intramolecular reactive sites that were approximately 4 Å away. All other potential reactors (both intramolecular and intermolecular) were at least 0.4–0.7 Å away. The shortest path for the intermolecular reaction was found to always lie in one crystallographic direction (x, $^1/_2 - y$, $^1/_2 + y$).

ESR Study. An investigation into the nature of the propagating species in the solid-state polymerization was made through the use of ESR techniques. Irradiation of the monomer was performed at −196 °C, and the sample was warmed to room temperature. The ESR spectra of the polycrystalline sample recorded 1 day, 1 week, and 1 month after irradiation are reproduced in Figure 5. Computer simulation nearly reproduced the signal when it was estimated that the radical was interacting with three equivalent and two nonequivalent hydrogens with the following hyperfine coupling constants: $a_\beta(\mathrm{CH_3}) = 20$ G, $a_\beta(\mathrm{CH}) = 9$ G, and $a_\beta(\mathrm{CH}) = 35$ G. The intensities of the fifth, sixth, and ninth lines from the left of the spectrum were, however, never quite reproduced in the simulation. One possible explanation was the likelihood that more than one radical species contributed to the spectrum. The primary species expected from the irradiation are shown as structures 2–4. While differentiation between the first two might be fairly difficult unless the coupling constants of the β hydrogens were widely different for the two intermediates, the third, however, would be expected to give a triplet ESR spectrum with 1:2:1 intensities. It was decided that more information concerning the formation of these species could be obtained by ESR measurements on an irradiated single crystal at various temperatures between and including −196 and +20 °C. Research on this question is being continued.



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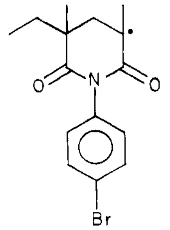

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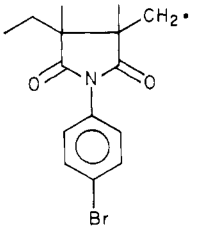

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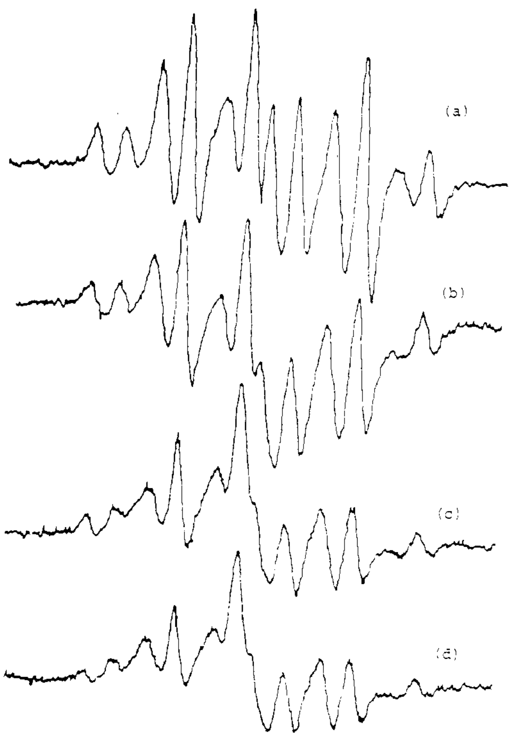

Figure 5. ESR spectra of γ-irradiated *N*-(*p*-bromphenyl)dimethacrylamide: (a) 1 day after irradiation; (b) 1 week after irradiation; (c) 1 month after irradiation; (d) 4 days after opening to air.

The radical centers generated by the irradiation were quite stable over a long period of time, though there was an obvious loss in intensity and fine structure of the peaks. Exposure to air for 4 days did not appreciably affect the spectrum, which was consistent with the probable slow diffusion of oxygen through the crystal lattice.

Solution Investigation. IR Analysis. Since the wavelengths at which carbonyl stretching vibrations occur

Table X
Solution Polymerizations of *N*-(*p*-Bromophenyl)dimethacrylamide

solvent[a]	ϵ[b]	*T*, °C	reaction time, h	conversion, %	5-membered,[c] %	6-membered,[d] %
benzene	2.274	58	24	34.0	80	20
benzene	2.274	114	24	27.6	42	58
dimethylformamide	36.71	56	22	23.2	81	19

[a] [M] = 0.5 M; AIBN = 1%. [b] Dielectric constant at 25 °C. [c] Determined by planimetry of the methyl resonances ^{1}H NMR at δ 1.5 [d] Determined by planimetry of the methyl resonances at δ 1.7.

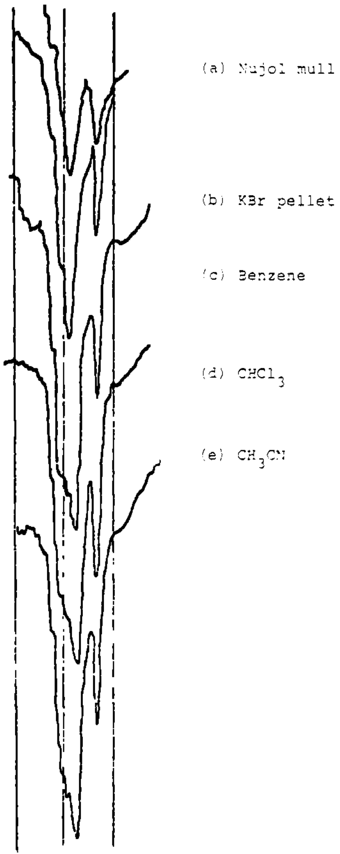

Figure 6. Infrared spectra of *N*-(*p*-bromophenyl)dimethacrylamide in (a) Nujol mull, (b) KBr pellet, (c) benzene (0.24 M), (d) chloroform (0.24 M), and (e) acetonitrile (0.24 M).

are so sensitive to the environment of the chromophore, the IR spectra of the monomer were compared when the monomer was in the solid phase (KBr pellet and Nujol mull) and in solution in benzene (dielectric constant ϵ = 2.274), chloroform (ϵ = 4.726), and acetonitrile (ϵ = 38.8). The absorption range, 1600–1800 cm^{-1}, over which carbonyl stretching vibrations generally occur, is shown for each of the spectra in Figure 6.

Since there was no obvious change in the IR spectra of the solid monomer in the two media, it was concluded that conformational changes were not induced by the pellet-grinding process[26] and that the orientation of the imide carbonyls as determined by the X-ray diffraction study was characterized by the carbonyl stretching frequencies shown in Figure 6a,b. A new strong absorption at 1670 cm^{-1} appeared in all three solution spectra, which could be indicative of conformational changes occurring during the dissolution of the monomer. The spectra were essentially unchanged by an increase in polarity of the medium, indicating that interactions within the monomer are stronger than those between the monomer and the solvent.

Polymerization Studies. The free radical initiated polymerization of *N*-phenyldimethacrylamide has been reported elsewhere.[13,25,27] The effect of reaction conditions such as polarity of the solvent and the polymerization temperature on the structure of poly[*N*-(*p*-bromophenyl)dimethacrylamide] is reported here.

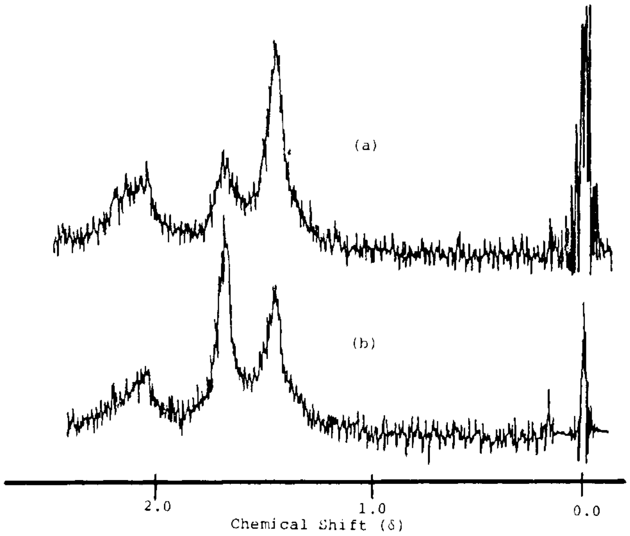

Figure 7. ^{1}H NMR spectra (100 MHz) of poly[*N*-(*p*-bromophenyl)dimethacrylamide] polymerized in benzene at (a) 58 and (b) 114 °C. The spectrum was run at 150 °C; solvent was nitrobenzene.

In all the polymerizations performed, a linear soluble polymer was obtained. Spectral investigation revealed no residual unsaturation in the isolated polymers. The effect of temperature on the polymer structure was investigated by performing the AIBN-initiated reactions in benzene in sealed evacuated polymerization tubes. The temperature were maintained at 58 and 114 °C for 24 h. The upfield regions of the high-resolution ^{1}H NMR spectra of the polymers are given in Figure 7. Comparison of the methyl shifts at δ 1.5 and 1.7 with those reported earlier[13] for poly(*N*-phenyldimethacrylamide) indicated that a large percentage of five-membered ring was formed in the polymerization at lower temperature. A significant increase in the reaction temperature, however, resulted in a stronger preference for the formation of six-membered ring.

Polymerization in the more polar dimethylformamide (DMF) also resulted in a linear soluble polymer with no detectable residual unsaturation. The ^{1}H NMR analysis indicated that primarily five-membered rings were formed at lower reaction temperatures. Molecular weight distributions as determined by gel permeation chromatography (GPC) were almost identical for the three solution polymers. The polymerization conditions and results are summarized in Table X.

Discussion

Solid-state polymerization of *N*-(*p*-bromophenyl)dimethacrylamide was accomplished in 16% conversion via cobalt-60 irradiation. ESR measurements on an irradiated sample indicated that 2 Mrd was sufficient to generate radical centers; however, this dose was not sufficient for polymer formation. Irradiation and subsequent postpolymerization was effected at least 75 °C below the monomer melting point (see Experimental Section), thus decreasing the probability that zone melting would occur at the polymer interface. In zone melting, the polymer formed may be the result of liquid rather than solid-state reaction. The large yields obtained by Azori et al.[28] in the "solid-state" polymerization of *N*-phenyldimethacrylamide performed at 5 °C below the monomer's melting point were quite likely the results of similar transitions and possibly were not solid-state processes at all.

Spectral measurement indicated that the monomer polymerized to a linear soluble polymer with no detectable residual unsaturation. Estimation of cyclization by 100-MHz NMR indicated the structure to consist of 60% five-membered rings and 40% six-membered rings. Although the polymerization was apparently specific with regard to the cyclization reaction, the ring sizes formed appeared to be the result of a more random selection.

Diffusion of reacting species toward each other is a prerequisite for chemical reaction; motion of some type must therefore occur after initiation for the reaction to propagate in the solid state. The feasibility of solid-state polymerization processes therefore hinges more on the spatial relationships of the reactive groups in the crystal lattice than on their chemical reactivity. Schmidt and co-workers[29-31] have studied the relationship between lattice geometry and photodimerization of olefins and have derived a general rule that photopolymerization occurs only in those crystals in which the distance between the adjacent double bonds is ≤ 4 Å. For longer distances, the compound was light stable. Hirshfeld and Schmidt[32] extended the postulate to compounds that undergo solid-state polymerization for which crystallographic data were available. Their survey also supported the postulate that the polymerization reaction would be possible only if the crystal structure afforded such close contact between the reacting centers.

Examination of the ORTEP drawing of Figure 3 and comparison of the relative positions of the symmetry-related monomers in the crystal lattice revealed that the solid-state cyclopolymerization was very much influenced by the geometry of the lattice. The two reacting double bonds, however, were not oriented in a manner that would favor a nonconjugated through-space interaction. A comparison of the intramolecular and intermolecular distances between the carbon atoms involved in the polymerization revealed a consistent trend, however, that emphasized the influence of the lattice. As shown in Table IX, all the carbons in the double bonds had at least one and, in some cases, two routes for intramolecular propagation (cyclization) that were ≤ 4 Å. All other routes were at least 0.4–0.7 Å longer. Based on the rule of Schmidt, this would probably mean that no reaction occurred by these alternate routes.

As indicated earlier, a high degree of cyclization was observed in the polymerization. The reactive species, whether it be an ion or radical, would have a different configuration than it had previously. These changes are unpredictable, and it would be impossible to determine precisely the exact relative orientation of the species to the other reaction sites. Since the atoms must diffuse from a distance of ~ 4 Å apart to the distance of a carbon–carbon single bond (~ 1.4 Å), it is also highly improbable that their original orientation would be maintained through such a displacement. Therefore, correlations of the crystallographically determined atomic positions with the ring sizes in the polymer backbone would be unfounded. However, in all cases the difference between the shortest intramolecular route and the shortest intermolecular one (0.4–0.7 Å) was so large that it is reasonable to predict that these initial orientation changes would not drastically change this trend. Therefore, it appears that the monomer crystallizes in a conformation that would favor cyclization over the intermolecular propagation as long as the crystal geometry controls the course of the reaction.

The intermolecular distances calculated are quite large; on this basis, the propagation reaction would be predicted to be slow (see Table IX), as was observed (see Experimental Section). Once an addition did occur, however, the heat of polymerization released might contribute to the molecular mobility. Even with these probable favorable contributions, the degree of polymerization was only 11 or 12, indicating that these polymerization processes were not easily accomplished.[33] This could be due to the large distances through which the reacting sites had to diffuse before reaction could occur.

The ESR study of the irradiated monomer indicated that radical centers were generated. The complexity of the signal indicated the probable presence of more than one species. The slight changes in the intensities and fine structure of the spectra with time could be attributed to propagation occurring or radical recombinations or terminations. However, the persistence and strength of the signal over such a long time was indicative of the restricted mobility of the monomers in the crystal lattice.

The monomer's position in the crystal lattice has been determined fairly precisely as well as the crystallographic direction through which propagation should initially occur; it should, therefore, be possible to monitor changes in the crystal lattice due to the polymerization processes. Generation of active centers in a single crystal by γ irradiation at −196 °C has been shown to result in the formation of radical sites that are precisely oriented with respect to the crystal axes.[34,35] Examination of the ESR signal from irradiated *N*-(*p*-bromophenyl)dimethacrylamide when each of the three axes were parallel to the magnetic field of the spectrometer should, therefore, reveal an orientation effect (anisotropy) in the spectra. Investigation into these possibilities is presently being conducted.

The conformation of a molecule in the solid state can be quite different from that which it may assume in solution. The increased capability of reacting species to diffuse to one another can result in quite a different reaction in the solution polymerization. As a means of investigating possible conformational changes of the molecule upon dissolution, the IR spectra of the monomer in the solid and solution states were recorded.

The three solution spectra (see Figure 6) were characterized by a new absorption band at 1670 cm^{-1}. This band could be related to a change in conformation of the imide group. Once the restraints of the crystal lattice are lifted and rotations around single bonds can occur, the monomer could orient so that the carbonyls would be in a different environment than they were in the crystal phase. The stretching vibrations of the carbonyls in this new environment should occur at a new wavelength; hence, the new absorption band.

The solution spectra of the monomer showed no obvious changes when the polarity of the medium was increased. This would be consistent with the interactions within the monomer molecule being stronger than those between the monomer and the solvent. These results are similar to those reported by Boyarchuk[36] on the rotational isomerism of imide groups. Diisobutyramide and dimethacrylamide exhibited changes in their IR spectra attributable to conformational changes, but variation in solvent polarity had little effect on the spectra of *N*-methyldimethacrylamide. It was concluded that the steric factors disrupting the coplanarity of the imide group and an increase in the van der Waals radius of the nitrogen substituent could disrupt totally a planar conformation of the molecule. Similarly, such conformational changes could be favored enough in *N*-(*p*-bromophenyl)dimethacrylamide so that the change of the medium (from $\epsilon = 2$ to $\epsilon = 39$) did not induce orientational changes large enough to be detectable.

The free radical initiated polymerizations yielded polymers whose structures were not affected by the polarity of the solvent. In both benzene and DMF, there was a 4:1 preference for the formation of five-membered instead of six-membered rings at lower reaction temperatures. Although this is contrary to initial reports favoring formation of six-membered ring in the cyclopolymer,[37] additional evidence has been more recently provided that quite a few of these polymerizations proceed under kinetic control with formation of the thermodynamically less stable intermediate, the primary rather than the secondary or tertiary cyclized radical.[38,39]

Predictions concerning kinetic or thermodynamic control of the cyclization cannot, however, be made entirely from the stability of the intermediate radical formed. When the ring formed in the cyclization reaction is a heterocycle or contains an sp^2-hybridized atom, the geometric stability of the ring itself may be a controlling factor. The ring formed in the cyclopolymerization of *N*-(*p*-bromophenyl)dimethacrylamide contained both a heteroatom (nitrogen) and two sp^2-hybridized carbons. The large percentages of five-membered rings formed at low polymerization temperature could not, therefore, be assigned a priori to the formation of the more or less stable isomer in the polymerization step, even though the formation of a primary radical intermediate is generally considered to be less favored thermodynamically than that of secondary or tertiary radicals. Significantly increasing the reaction temperature of the polymerization in benzene, however, increased considerably the percentage of six-membered ring, which led to the conclusion that it was the product favored thermodynamically. Therefore, it is likely that the low-temperature products are the result of the faster cyclization process.

It is rather difficult to explain why the propagating radical adds more rapidly to the substituted end of the double bond than to the terminal end. Obviously the stability of the radical formed in the cyclization step is not the sole deciding factor. The direction of cyclization has been explained by electronic[3,40] and steric[41,42] interactions, but it has also been suggested[43] that more conformations are available for the formation of a cyclopentylmethyl than for a cyclohexyl ring. In a review by Struble, Beckwith, and Gream,[44] it was proposed that the interaction of the unpaired electron with the lowest unoccupied orbital (LUMO) of the unsaturated double bond determined the course of the free radical addition reaction. It was expected that bond formation would occur at that end of the double bond more readily approached vertically by the attacking radical.

Preliminary results from a quantum mechanical analysis of the monomer indicate that the steric interactions severely limit the number of energetically favorable conformations available to *N*-(*p*-bromophenyl)dimethacrylamide. Rotations around single bonds should be difficult, and it is not improbable that one of the methacryl groups might approximately maintain the same orientation until approached by the reacting species, which could favor the formation of one ring size over another in the cyclopolymerization reaction.

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Supplementary Material Available: Materials and Equipment, observed and calculated structure factors for *N*-(*p*-bromophenyl)dimethacrylamide, and a packing diagram of the unit cell of *N*-(*p*-bromophenyl)dimethacrylamide with monomers above, below, and to either side of the unit cell (28 pages). Ordering information is given on any current masthead page.

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Preferred Conformations of Linear Homooligoprolines. *N-tert*-Butyloxycarbonyl-D-prolyl-D-prolyl-L-proline[1]

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ABSTRACT: An analysis of the preferred conformations of *N-tert*-butyloxycarbonyl-D-prolyl-D-prolyl-L-proline was performed in the solid state and in solution using X-ray diffraction and infrared absorption. In the solid state the stereosequence of the ω angles is cis,trans,cis and that of the ϕ, ψ angles F*,F*,F. The molecules do not form an intramolecularly hydrogen-bonded oxy-C_{10} peptide conformation, but rather they are held together through intermolecular O–H···O=C (Pro_1–Pro_2 peptide carbonyl) bonds. In solvents of low polarity the following are observed: (i) in concentrated solution the type of association which occurs is different from that found in the solid state and (ii) in dilute solution there is no evidence for the onset of intramolecularly hydrogen-bonded forms. In solvents with strong hydrogen-bonding acceptor and donor properties only solvated species are seen.

In 1974, on the basis of infrared (IR) absorption evidence, Deber[3] proposed the presence of oxy analogues of the 4←1 intramolecularly hydrogen-bonded peptide conformations (β turns, C_{10} ring structures)[4,5] in the solid state for *t*-Boc-Gly-L-Pro-OH (*t*-Boc = *tert*-butyloxycarbonyl), *t*-Boc-L-Pro-Gly-OH, *t*-Boc-L-Pro-D-Pro-OH, and *t*-Boc-L-Pro-L-Pro-L-Pro-D-Pro-OH.

Since purely on the basis of the IR absorption data it is impossible to rule out unequivocally intermolecular hydrogen-bonding effects in the crystals of these acids, following Deber's suggestion[3] we undertook an X-ray diffraction analysis of the four aforementioned oligopeptides. The results already published indicate that the molecules of *t*-Boc-L-Pro-Gly-OH,[6] *t*-Boc-Gly-L-Pro-OH,[7] and *t*-Boc-L-Pro-D-Pro-OH[8] do not adopt an oxy-C_{10} conformation but rather that they are held together through intermolecular O–H···O=C hydrogen bonds, with either the urethane or the peptide carbonyl group acting as the acceptor.

In this paper we describe first the solid-state preferred conformation of the enantiomer of the last peptide examined by Deber,[3] namely, *t*-Boc-D-Pro-D-Pro-L-Pro-OH, using IR absorption and X-ray diffraction. The ϕ, ψ conformational region (A or F),[9] urethane and peptide bond conformations (cis or trans),[10–12] pyrrolidine puckering (A or B; C_2 or C_s symmetry),[13,14] and hydrogen bond (inter- or intramolecular, with urethane, peptide, or acid carbonyl as the acceptor)[4,5] will be discussed. The IR absorption properties of *t*-Boc-D-Pro-D-Pro-L-Pro-OH in solvents of widely divergent polarity and hydrogen-bonding capability are also reported. The conclusions are facilitated by comparison with the results obtained for the tripeptide benzyl ester. The trans-II′ oxy-C_{10} structure for a D-Pro-L-Pro sequence occurring at the C terminus of a polypeptide chain is illustrated in Figure 1.

This study is also part of our continuing, systematic analysis of the conformation of linear homooligoprolines (to the tetrapeptide) having all possible chiral sequences and different N-protecting and C-terminal groups.[8,15,16]

Experimental Section

Synthesis of Peptides. *t*-Boc-D-Pro-D-Pro-L-Pro-OH was prepared by catalytic (Pd/C) hydrogenation of *t*-Boc-D-Pro-D-Pro-L-Pro-OBzl (OBzl = benzyloxy) in *tert*-butyl alcohol: mp 202–203 °C, after recrystallization from methanol–diethyl ether; $[\alpha]^{20}{}_D$ +40.5° (*c* 1.45; methanol); TLC, R_{f_1} 0.50 (SiO_2, Merck; 3:1:1 *n*-butyl alcohol–water–acetic acid), R_{f_2} 0.10 (SiO_2, Merck; 9:1 chloroform–ethanol). Anal. Calcd for $C_{20}H_{31}N_3O_6$: C, 58.7; H, 7.6; N, 10.3. Found: C, 58.1; H, 7.6; N, 10.2.

In turn, *t*-Boc-D-Pro-D-Pro-L-Pro-OBzl was prepared from *t*-Boc-D-Pro-D-Pro-OH[8] and HCl·H-Pro-OBzl in anhydrous chloroform in the presence of *N*-methylmorpholine and isobutyl chloroformate:[17] oil, after precipitation from ethyl acetate–petroleum ether; $[\alpha]^{20}{}_D$ +26.9° (*c* 1.2; methanol); R_{f_1} 0.75; R_{f_2} 0.90. Anal. Calcd for $C_{27}H_{37}N_3O_6$: C, 64.9; H, 7.5; N, 8.4. Found: C, 64.2; H, 7.4; N, 8.3.

Infrared Absorption. Infrared absorption spectra were recorded with a Perkin-Elmer Model 580 spectrophotometer. For the solid-state measurements the KBr disk technique was used. For the solution measurements 0.2- and 0.1-mm cells with CaF_2 windows were employed. Trimethyl phosphate (TMP), methylene-d_2 chloride (99.8% D), deuteriochloroform (99.8% D), deuterium oxide (99.9% D), *p*-dioxane, and acetonitrile were purchased from Merck. The band positions are accurate to ±1 cm^{-1}.

X-ray Diffraction. Crystals of *t*-Boc-D-Pro-D-Pro-L-Pro-OH in the form of colorless plates were grown from 1:1 methanol–acetone solution.

A CAD4 Enraf-Nonius diffractometer of the Centro di Metodologie Chimico Fisiche of the University of Naples, equipped with PDP 8/E and PDP 11/34 digital computers, was used for the data collection, structure determination, and refinement. The SDP (structure determination program) package of crystallographic programs was used in all stages of calculations. The

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