(100–300 Mrad), depolymerization can occur without significant changes in the melting point. For example, Figure 7 shows results of experiments in which two samples undergoing postirradiation depolymerization at room temperature were examined by DTA after various times. The results obtained after a dose of 138 Mrad in air show that a loss of 8% in weight is accompanied by a change in melting point from 141 to 143°. Another sample which had received the same dose under vacuum lost 3% in weight with a change in melting point from 142° to 143°. These results, along with ones obtained after a dose of 101 Mrad, show that these changes in melting point are unimportant relative to the large depressions due to irradiation (*cf.* Figure 4).

One clue to the physical nature of radiation damage has been obtained by Jaffe and Wunderlich.[4] These authors calculated values of density changes from measurements of refractive index. A decrease from 1.480 to 1.449 g cm^{-3} was calculated after a dose of 45 Mrad. It was suggested that this was due to the formation of holes and disordering. This large decrease which is equivalent to a loss of 2% by weight is presumably due, largely, to depolymerization. Possibly, the holes do not affect melting behavior through being annealed during the DTA scan.

Conclusion

(1) After doses in the range 100–300 Mrad, under vacuum, the depression of the melting point of polyoxymethylene lies in the range 0.115 to 0.160°C/Mrad. This value is in agreement with a value of 0.154°C/Mrad deduced from data reported by Jaffe and Wunderlich for a sample irradiated in air.

(2) Substitution of the values 0.115 and 0.160°C/Mrad in an equation derived from the Clapeyron–Clausius equation, along with a value for the enthalpy of fusion of 53.3 cal/g, gives values for units excluded from the crystal lattice by irradiation of $G(-\text{units}) \simeq 17$ to 23.

(3) A value of G(units chemically changed) $\simeq$ G(fractures) + 2G(cross-links = $-CH_2CH_2-$ groups) = 24 ± 1.0 was calculated from chemical analyses reported by Fischer and Langbein for polyoxymethylene irradiated under vacuum at dose rates three orders of magnitude higher than in the cryoscopical studies.

(4) There is good agreement between the chemical and cryoscopic studies but the former relate to doses documented up to 100 Mrad whereas the latter have been demonstrated only for doses in the range 100–300 Mrad.

(5) At doses <100 Mrad the cryoscopic methods give values of G(units) > G(units chemically changed). It is suggested that a complication is involved at low doses because of thermal instability of the irradiated polymer. At doses >100 Mrad a sufficient amount of thermally stable polymer is formed to allow monitoring of the melting point.

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Cocrystallization in Polyamides from Bis(4-aminocyclohexyl)methane

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ABSTRACT: A study was made of the crystallinity of polyamide copolymers derived from mixtures of bis(4-aminocyclohexyl)methane (PACM) and various acyclic diamines with dodecanedioic acid or suberic acid. The highest degree of cocrystallization was observed when 1,9-nonanediamine or 5-methyl-1,9-nonanediamine was used as the second diamine component. Evidence of this was obtained from plots of crystalline melting point *vs.* composition and from heats of fusion of copolymers derived from equimolar mixtures of diamines. All α,ω straight chain diamines in the range of 6 to 12 carbon atoms showed varying degrees of crystallinity retention, with those longer than nine carbon atoms exhibiting greater retention than those shorter. X-Ray diffraction data indicated that while 1,12-dodecanediamine derived copolymers cocrystallize, those obtained using 1,6-hexanediamine do not. Other ring-containing monomers (*e.g*, 1,4-bis(aminomethyl)cyclohexane, 1,3-bis(4-piperidyl)propane, and *p,p′*-methylenedianiline) did not cocrystallize with PACM when used to prepare polyamide copolymers.

The ability of polymer repeat units to cocrystallize has been a matter of considerable interest and importance in the area of polyamides derived from alicyclic diamines, due largely to the presence of cis and trans isomers in these systems and their effect on polymer properties. Previous work has shown[1] that *cis*- and *trans*-1,4-bis(aminomethyl)cyclohexane cocrystallize with very little lattice distortion when polymerized with a dicarboxylic acid having from 6 to 12 carbon atoms. In similar polyamides derived from bis(4-aminocyclohexyl)methane, the *trans,trans* and *cis,trans* isomers cocrystallize with significant lattice distortion.[2,3] The behavior of copolymer systems derived from these di-

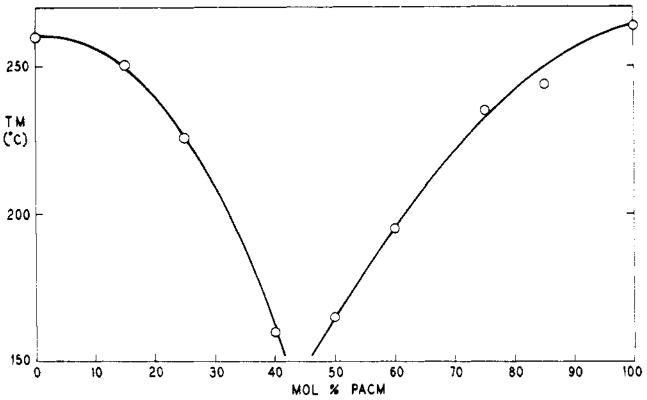

Figure 1. Crystalline melting point *vs.* composition for PACM/BAMCH-12 copolymers.

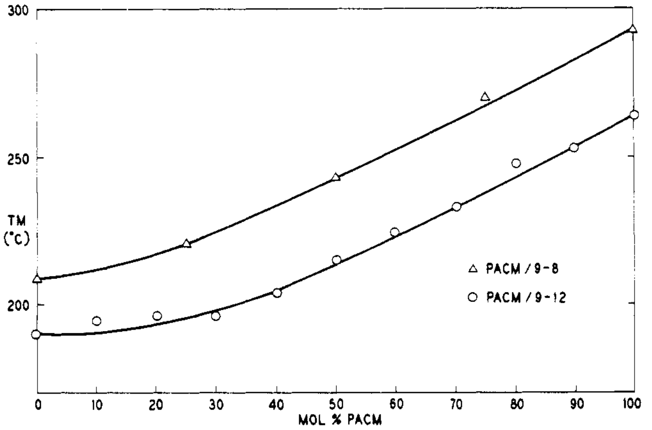

Figure 2. Crystalline melting point *vs.* composition for PACM/9-8 and 12 copolymers.

carboxylic acids and mixtures of bis(4-aminocyclohexyl)methane and α,ω-acyclicdiamines, with respect to crystallinity and fiber properties, was of interest and is the subject of this paper.

Results and Discussion

Retention of crystallinity in copolymers is usually described as isomorphism (isomorphous replacement) or cocrystallization. These terms have been used in various ways in the polymer literature, sometimes interchangeably[4] and other times as a means of differentiating[5] between the behavior of various copolymer systems. In this discussion, isomorphous replacement refers to a complete lack of change in crystal lattice spacings of a copolymer system in going from one homopolymer to another, obviously requiring the crystal structure (unit cell dimensions and crystal lattice) of the two homopolymers to be the same. Cocrystallization describes the continuous change of one crystal structure to another in a copolymer system in which crystallinity is maintained throughout the entire range of compositions.

Isomorphous replacement can only be detected by a method which characterizes crystal structure (*e.g.*, X-ray diffraction). Information concerning cocrystallization, however, can be obtained from a variety of sources. Both X-ray diffraction and differential thermal analysis (DTA) can be used to establish the existence of crystallinity in a copolymer series. Trends in crystalline melting points and heats of fusion give an indication of how well crystallinity is retained (degree of cocrystallization).

Table I
Crystallinity in PACM: Comonomer (50/50)-12 Polyamides

Comonomer	ΔH, cal/g[a]	T_m, deg[b,c]	T_g, deg[b]	η_{inh}[d]
None	6.8	265	134	0.85
1,6-Hexanediamine	Low[e]	200	76	0.96
1,8-Octanediamine	6.4	209	74	0.89
1,9-Nonanediamine	11.7	218	70	0.74
1,10-Decanediamine	8.1	210	69	0.79
1,12-Dodecanediamine	6.8	196	66	0.96
5-Methyl-1,9-nonanediamine	7.3	202	68	0.97
1,3-Bis(4-piperidyl)-propane	Low[e]	192	70	1.01
p,p'-Methylenedianiline	0	(185)	110	0.51
1,4-Bis(aminomethyl)-cyclohexane	0	(165)	99	0.68
1,4-Bis(2-aminoethyl)-cyclohexane	0	(175)	93	0.86

[a] Heat of fusion determined by quantitative DTA. [b] Determined on premelted and quenched samples by DTA. [c] Values shown in parentheses are polymer melt temperatures of materials showing no crystallinity by DTA. [d] Measured on 0.5% solutions in *m*-cresol at 30°. [e] Small, ill-defined melting endotherm.

Crystalline Melting Temperature *vs.* Composition. The absence of a minimum in a plot of melting point *vs.* composition has long been a criterion for "cocrystallization" in copolymer systems. Although Trantor has shown[6] that "cocrystallizing" systems can exhibit a minimum in softening temperature, crystalline melting point data do provide information about crystallinity retention or disruption by a comonomer. A plot of crystalline melting point (T_m) *vs.* composition for a series of copolymers prepared from mixtures of bis(4-aminocyclohexyl)methane (PACM; 54% trans,trans; 39% cis,trans; 7% cis,cis; equilibrium mixture of isomers) and 1,4-bis(aminomethyl)cyclohexane (BAMCH; 74% trans, 26% cis) with dodecanedioic acid is shown in Figure 1. It is typical of systems which do not cocrystallize, amorphous products being obtained in the 60:40–40:60 molar ratio range. The values shown in Figure 1 for these intermediate compositions are polymer melt temperatures[7] of materials showing no crystalline melting point by DTA. In contrast, copolymers derived from PACM and 1,9-nonanediamine with either suberic or dodecanedioic acid (Figure 2) were found to be crystalline throughout the range of compositions, indicating that this alicyclic diamine–acyclic diamine combination, each having a nine-carbon chain separating the amine groups, is an example of a cocrystallizing system. The absence of a minimum in melting point is indicative of a high degree of crystallinity retention.

50:50 Copolymers as Crystallinity Indicators. The intermediate range of substitution (60:40–40:60) frequently provides a good indication of crystallinity retention in copolymers. This is particularly evident in Figures 1 and 2. A variety of diamine comonomers were used to replace 50 mol % of the PACM in a series of polyamides derived from dodecanedioic acid (Table I). Heats of fusion (Δ*H*) were determined by quantitative DTA and were measured, along with crystalline melting temperature (T_m) and glass transition temperature (T_g), on samples which had been premelted at 300° and quenched. The copolymers derived from acyclic diamines were all crystallizable materials. Crystallinity is at a maximum, as evidenced by both Δ*H* and T_m, in the copolymer from 1,9-nonanediamine. The degree of

Table II
Effect of PACM Incorporation on T_m of Dodecanediamides

Diamine	Homopolymer[a] T_m, deg[c]	Homopolymer[a] η_{inh}[d]	Copolymer[b] T_m, deg[c]	Copolymer[b] η_{inh}[d]
1,8-Octanediamine	201	1.64	197	1.35
1,9-Nonanediamine	190	0.61	195	0.65
1,10-Decanediamine	187	0.66	183	0.63
1,12-Dodecanediamine	186	0.74	180	1.19
5-Methyl-1,9-nonanediamine	161	1.00	166	1.01
1,3-Bis(4-piperidyl)propane	142	0.71	135	0.94

[a] Diamine-12 polyamide. [b] Diamine/PACM (90:10)-12 polyamide. [c] Determined by DTA on samples which had been premelted at 300° and quenched. [d] Measured on 0.5% solutions in *m*-cresol at 30°.

Table III
X-Ray Diffraction Patterns of PACM Copolymers[a]

Comonomer	Mole %	Lattice spacing, Å
None		4.60, 5.10
1,6-Hexanediamine	50	4.64 (d)[b]
	100	3.81, 4.23, 4.52
1,9-Nonanediamine	40	4.21
	60	4.18
	100	3.75, 4.04
1,12-Dodecanediamine	50	4.50
	100	3.72, 4.45
5-Methyl-1,9-nonanediamine	50	4.20, 4.50
	100	3.96, 4.44
1,3-Bis(4-piperidyl)propane	50	4.70 (d)[b]
	100	4.67, 5.12

[a] PACM/comonomer-12 polyamides. [b] Showed only a diffuse pattern characteristic of amorphous polymer.

Table IV
Polyamide Fiber[a] Properties

Polymer	Tenacity,[b] gpd	Work recovery,[c] %	Wet modulus[d] (60°), gpd	Disperse[e] dyeability, *K/S*	Wet T_g,[f] deg
PACM-12	4.2	72	22	1.8	110
Nylon 66	6.7	37	5.5	18	−15
PACM/9-12[g]	5.1	73	24	18	81
PACM/BAMCH-12[h]	3.7	76	17	>10	81

[a] Filaments were melt spun and fully drawn. [b] ASTM 2256-69, breaking strength in grams of a 9000-m filament weighing 1 g. [c] From 3% elongation. [d] ASTM 2256-69, initial modulus of fiber measured in water at 60°. [e] Dyed at the boil in aqueous Celanthrene Fast Blue 2G (1.5%). *K/S* values are proportional to dye uptake and are described in *J. Opt. Soc. Amer.*, 38, 1067 (1948). [f] Reference 10 describes the relationship between wet and dry T_g. [g] Polyamide from an 80/20 mol % mixture of PACM and 1,9-nonanediamine with dodecanedioic acid. [h] Polyamide from an 80/20 mol % mixture of PACM and BAMCH with dodecanedioic acid.

crystallinity is particularly significant when compared with the heat of fusion of the homopolymer from 1,9-nonanediamine and dodecanedioic acid (11.4 cal/g).

As the chain length of the diamine comonomer is changed from the optimum value of nine-carbon atoms, increases cause less crystallinity disruption than decreases. In this series, T_g undergoes a definite decrease (76–66°) as the comonomer chain length is increased. The symmetrically substituted 5-methyl-1,9-nonanediamine also gave a copolymer retaining considerable crystallinity. None of the ring-containing monomers gave good retention at the 50 mol % level, including a nine-carbon chain piperidine derivative [1,3-bis(4-piperidyl)propane] and the aromatic analog of PACM (*p,p*′-methylenedianiline). This is taken as an indication that, in addition to repeat unit length (along the molecular axis), geometrical shape (three-dimensional) is an important criterion for cocrystallization.

Lower Melting Homopolymer Modification. Examination of T_m *vs.* composition curves reveals that substitution of a small amount of the higher melting component into the lower melting homopolymer distinguishes between systems which do and do not have a minimum in this relationship, not always evident in comparisons involving 50:50 copolymers. For this reason, a series of homopolymers with dodecanedioic acid and copolymers containing 10 mol % PACM were prepared (Table II) from some of the diamines shown in Table I, retaining various degrees of crystallinity. The only diamines found to give an increase in T_m when PACM is introduced are 1,9-nonanediamine and its 5-methyl derivative. In each of the other cases, T_m underwent a 4–7° decrease, an indication of crystallinity disruption.

X-Ray Examination of Copolymers. Since X-ray diffraction data give the clearest picture of changes in crystallinity (*e.g.*, lattice distortion and new crystal structures), several of the copolymer systems were examined by this technique (Table III). Both 1,6-hexanediamine and 1,3-bis(4-piperidyl)propane gave 50:50 copolymers with PACM which appeared highly amorphous by their diffraction pattern and, for this reason, are not cocrystallizing systems. It is interesting that the two homopolymers from PACM and 1,3-bis(4-piperidyl)propane with dodecanedioic acid have quite similar lattice spacings. Copolymers derived from PACM and either 1,9-nonanediamine, 1,12-dodecanediamine, or 5-methyl-1,9-nonanediamine all showed crystalline diffraction patterns and had spacings which underwent a gradual change from one homopolymer to the other. Since in all cases the homopolymer crystal structures were different, this behavior is characteristic of cocrystallizing systems and not isomorphous replacement.

Effect of Diamine Structure on Fiber Properties. The polyamide from PACM and dodecanedioic acid has an unusually high T_g (130–150°) due to the high concentration of ring structures in its repeat unit. This feature is largely responsible for the good washer–dryer performance and wrinkle resistance which fibers derived from this polyamide exhibit. It also results in poor dyeability in boiling aqueous systems. It has been found[8,9] that copolymers derived from the proper mixture of PACM and comonomeric diamines have glass transition temperatures in a range (70–90° when measured in water[10]) which combines the good wash-wear properties of a high T_g polyamide with the easy dyeability of a low T_g polyamide (*e.g.*, Nylon 66). A comparison of two copolymers, described previously, with PACM-12 and Nylon 66 is given in Table IV. The PACM homopolymer is characterized by high work recovery, indicative of good wrinkle resistance, and a high initial modulus in hot water, indicative of good washer–dryer performance. Its high T_g also results in poor dye uptake from an aqueous bath at the boil (low K/S). The two copolymers have T_g's in the range described previously and exhibit a desirable combination of performance and dyeability. The benefits derived from cocrystallization are clearly evident in comparing the crystallinity-related properties (tenacity and wet modulus) of the two copolymer fibers.

Experimental Section

Monomers. The diamines were vacuum distilled prior to use with the exception of *p,p'*-methylenedianiline, which was decolorized and recrystallized from benzene, and 1,6-hexanediamine (Eastman) and 1,3-bis(4-piperidyl)propane (Reilly), which were used as obtained. Dodecanedioic acid (Chemische Werkes Huls AG) and suberic acid (Aldrich) were used as obtained.

Polymers. The polyamides were prepared by conventional melt polymerizations involving equimolar diamine–diacid mixtures. Typical conditions involved a 2.5-hr heat up to a final temperature of 320°, 1 hr at 320° under 15–20 psig N_2, 1 hr at 320° under a slow N_2 flush, and 1 hr at 320°C at 30 mm Hg. Glass reactors prepared from ball/socket joint glass tubing were used, connected by rubber tubing to a manifold supplying N_2 and a vacuum.

Measurements. Inherent viscosities were measured in *m*-cresol on 0.5% solutions at 30°. Polymer melt temperatures,[7] reported for amorphous polymers, were determined on a heated brass rod with a temperature gradient (modified "Dennis bar").

The differential thermal analysis measurements were performed using a Du Pont Model 900 utilizing a DSC cell (constantan disk). The quantitative data were recorded on a time base Hewlett-Packard Model 7128A with a disk integrator. The samples (20 mg) were premelted at 300° for 3 min and quenched. The heat up was carried out at 10°/min under a helium atmosphere using an empty pan reference.

The X-ray diffraction data were obtained using a Norelco X-ray diffractometer with pulse height analyzer and a diffracted beam graphite monochrometer. Specimens were compression molded at 265° and cooled to 100° at a rate of 2°/min.

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Notes

Microprobe Analysis of Polystyrene-Attached Catalysts

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In the past few years, research directed toward the preparations and uses of polymer-attached catalysts has developed rapidly.[1-5] These catalysts combine many of the best features of "homogeneous" with the ease of use of "heterogeneous" catalysts. It is becoming apparent that these catalysts retain their "homogeneous" character when examined on a molecular basis but are heterogeneous when considered on a functional basis. The major portion of the research to date has been directed toward the preparation and properties of d^8 complexes attached to polystyrene copolymer beads. One of the keys to understanding the properties of these catalysts, such as their size selectivity[2] and catalyst activation or deactivation,[4,5] is the determination of the distribution of the catalyst in the copolymer beads.

The electron probe microanalyzer provides a rapid nondestructive technique for such determinations.[6] The resolution (several microns) of this instrument is more than sufficient for the analysis of the polymer beads in question which are generally from 300 to 700 μ in diameter. Each element can be detected independently on the same sample.

Experimental Section

Samples of the functionalized copolymer were prepared as reported earlier.[2] Conditions and reaction times for the equilibration studies are summarized in Table I.

Table I
Summary Preparation of Beads

Complex used	Equiv Rh/ equiv P (on beads)	Equilibration time	% Rh (analysis)
RhL_3Cl	1.00	2 weeks	3.43[a]
$[RhCOE_2Cl]_2$	0.310	12 hours	2.08
$[RhCOE_2Cl]_2$	4.30	4 days	2.62

[a] This batch had a greater per cent substitution of P than the latter which were from the same batch of phosphinated beads.

Sample Preparation. Sections (2 to 4 in.) of 4 mm inside diameter glass tube were sealed at one end. The tubes were cleaned (KOH-EtOH; HNO_3; distilled water) and dried. Each tube was wet with epoxy release agent and suspended with the open end up. A small portion of mixed epoxy was placed in the bottom of the tube with a micropipet. A few beads were then added followed by enough epoxy to half-fill the tube. The epoxy and beads were gently mixed with a nichrome wire, and the epoxy was allowed to set.

The glass tube was carefully broken from around the epoxy rod. The rod was cut into sections 0.5 in. or less in length. A short rod containing beads was attached to a larger diameter epoxy rod (α-cyano acrylate glue) which was mounted in a microtome.

Sections were made at room temperature using a stainless steel knife and a very slow cutting stroke. Once the knife penetrated the rod to a depth of 1 to 2 mm it was necessary to hold the section against the knife with a flat edged dissecting instrument to prevent curling. Sections were cut at 7 to 10 μ. Thinner sections tended to shatter the beads.

Matrix sections were mounted on graphite disks or quartz plates. Any adhesive will work. α-Cyano acrylate cement, electronic tube coating (graphite base), and the sticky residue from pressing and then removing freezer tape on the plate were used. Disks or plates were covered with a thin film of graphite (from carbon arc under high vacuum). The sections with the maximum diameter were chosen to represent the cross section of the beads.

Spectroscopic Determinations. Spectra were run on an American Research Laboratories EMX-SM Microprobe. Beams of 20 and 15 kV at 0.05 μA were used. X-Ray intensities were measured from Rh L-α, P Kα, and Cl Kα line emission. X-Ray intensities were taken as a measure of the relative density of a given element