Table I
X-Ray Data for Poly-N^5-(3-hydroxypropyl)-L-glutamine (Orthorhombic Unit Cell a = 14.6; b = 12.3; c = 43.2 Å)

hkl	d_0, Å	d_c, Å	I_0[a]
	Equator		
100	14.6	14.60	vvs
010	12.30	12.30	s
210	6.30	6.28	m
120	5.65	5.67	mw
030	4.15	4.10	s
	8th Layer Line		
118	4.75	4.68	vs
208	4.32	4.34	m
028	4.03	4.06	m
	16th Layer Line		
0,2,16	2.43	2.47	w
0,3,16	2.24	2.25	w
	24th Layer Line		
1,3,24	1.63	1.64	w
	29th Layer Line		
0,0,29	1.49	14.9	s

[a] Abbreviations used: w, weak; m, medium; s, strong; vs, very strong; vvs, very very strong.

the value of 29 × 1.49 = 43.2 Å which represents the c parameter of the unit cell.

Among the equatorial reflections the two at 14.6 and 12.30 Å may be directly related to the distance between the helices. This is also supported by the increase of these spacings in swollen low-crystalline samples. In conclusion we found that all observed reflections can be indexed according to an orthorhombic unit cell with a = 14.6, b = 12.3, and c = 43.2 Å. Miller's indices are reported in Table I together with the calculated spacing d_c. The calculated density is $D_c = n1.15$ g cm^{-3} where n is the number of helices crossing the orthorhombic cell. Comparison with the observed density indicates that such a cell is crossed by one α-helix only. The difference of about 7% between the measured density and the calculated crystal density might not be remarkable were it not for the fact that the measured density is higher despite a substantial amorphous content of the samples as evidenced by halos in the diffraction patterns. This is, of course, an unsatisfactory situation and would normally be taken to imply that the structure under consideration is incorrect. Since there are strong indications that the chains in the polymer have the α-helical configuration it is desirable to examine possible alternative explanations of the density anomaly. One such explanation would be that the polymer contained a certain percentage of water, because stringent drying conditions have not been used; this appears particularly reasonable in view of the findings of Astbury et al.[8] that certain synthetic polypeptides crystallize with a half molecule of water per residue. A second possibility is that the amorphous regions of the polymer may contain some interchain hydrogen bonds. It may be considered that this interchain bonding would tend to pull the chains closer together and hence lead to the higher density in the amorphous regions. In addition the higher value of the measured density might come from absorption and/or adsorption of the heavier mixture component by the semicrystalline sample,[9] or, alternatively, this would be an instance of a real anomaly as has been proposed for poly(γ-methyl L-glutamate).[10] Nevertheless, it is our feeling that this discrepancy appears to be outside the limits of experimental errors.

The reflections of the lower order layer lines appear to be broad. This suggests a disordered crystalline structure in which α-helical chains are packed parallel to each other and in an orthorhombic array, but randomly arranged along and about their lengths. Such disorder would lead to the appearance of sharp spectra for truly equatorial spacings and continuous intensity distribution on the other layer lines.[11]

Taking into account the possibility of correlating the polypeptide conformation in the solid state and in solution, the present results strongly indicate that PHPG in solution assumes the α-helical conformation.

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Glass Transition Temperatures of Regularly Alternating Acrylonitrile–Vinyl Acetate Copolymers

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It has been suggested recently[1–5] that the conformational entropy may be used, as a parameter characterizing the intramolecular polymer chain flexibility, to understand the sequence distribution–glass transition effects observed[6] in copolymers. Conformational entropies calculated for copolymers and their constituent homopolymer chains have been utilized[1–5] to predict deviations away from bulk additive sequence distribution–glass transition behavior described by relations such as the Fox equation.[7]

If the conformational entropy calculated for a given copolymer chain is greater (less) than the weighted sum of entropies calculated for the constituent homopolymer chains, then the glass transition temperature, T_g, is expected to be lower (higher) than the value predicted by the Fox equation or any other bulk additive relation. This approach has been applied[1–5] to a large number of copolymer systems and has been successful in predicting negative, positive, and no deviations from bulk additive T_g–sequence distribution behavior when they occur.

Chen[8] has recently described the synthesis of 1:1 regularly alternating copolymers of acrylonitrile (AN) and vinyl acetate (VA). Although few details were given, a T_g = 85 °C was reported for this regularly alternating copolymer system. This is ca. 20 °C above the T_g predicted by the Fox equation based on the T_g's of the AN (T_g = 105 °C) and VA (T_g = 30 °C) homopolymer chains.[9]

Since both AN and VA monomers had been treated in previous copolymer conformational entropy calculations[1–5] performed on the AN–styrene, AN–α-methylstyrene, and VA–vinyl chloride systems, some of the results of these previous calculations were supplemented by the present calculations performed on AN–VA dyads to obtain the conformational entropies of the regularly alternating copolymers. Chen was unable to determine the stereoregularity of the AN–VA copolymers she synthesized, so our calculations explicitly included the effect of stereoregularity upon the conformational entropy.

Details of the conformational entropy calculations have been described[1-5] in detail before. In the present calculation T = 67.5 °C, which is midway between the T_g's of AN and VA homopolymers,[9] and a dielectric constant[9] ϵ = 5 were employed.

Table I
Calculated Conformational Entropies of the Homo- and Regularly Alternating Copolymers of AN–VA

Polymer	Stereoregularity[a]	S,[b] eu/mol of backbone bonds
AN	I	1.270
VA	I	1.759
AN–VA	I	1.497
AN	S	1.298
VA	S	1.690
AN–VA	S	1.500
AN	A	1.270[c]
VA	A	1.790[c]
AN–VA	A	1.505[c]

[a] I ≡ isotactic, S ≡ syndiotactic, A ≡ atactic. [b] Calculated for chains of 500 bonds. [c] Average of 10 Monte Carlo generated chains, where the mean deviation from the average is less than 0.2%.

Table I presents the results of the entropy calculations performed on the isotactic, syndiotactic, and atactic homo- and regularly alternating copolymers of AN–VA. The entropies calculated for both the isotactic and atactic regularly alternating copolymers are less than half the sums of the isotactic and atactic homopolymers, while the syndiotactic copolymer entropy is nearly the same as half the sum of the syndiotactic homopolymer entropies.

On this basis the glass transition temperature of regularly alternating AN–VA copolymers would be expected to equal or exceed the T_g predicted by the Fox relation depending on stereoregularity. This is consistent with the observations of Chen who reports T_g = 85 °C for regularly alternating AN–VA copolymer of unspecified stereoregularity, though presumably atactic,[10] a value exceeding the T_g predicted by the Fox equation.

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(10) Because the AN–VA copolymers prepared by Chen[8] are amorphous, it is assumed they are stereochemically random, or atactic.

Photosensitized Degradations of Polystyrene and Poly-α-methylstyrene in Solution by Benzophenone

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Extensive studies on photochemistry of benzophenone (BP) have established that the excited BP molecule in the triplet state is capable of abstracting hydrogen atom from suitable hydrogen donor molecules (RH), which results in the formation of ketyl radical and R radical as follows:[1-8]

$$\mathrm{Ph_2CO} \xrightarrow{h\nu} {}^1\mathrm{Ph_2CO^*} \rightarrow {}^3\mathrm{Ph_2CO^*} \xrightarrow{\mathrm{RH}} \mathrm{Ph_2\dot{C}OH} + \mathrm{R}\cdot$$

In this paper, we wish to report the photosensitized degradations of polystyrene (PSt) and poly-α-methylstyrene (PMSt) in benzene solution which are initiated from hydrogen abstracted sites of polymer chains by photochemically excited BP.

PSt and PMSt were prepared at −78 °C by the use of boron trifluoride etherate as a catalyst. The polymers were purified by precipitation from benzene solution with methanol. The number-average molecular weights of PSt and PMSt thus obtained were 6.5 × 10^5 and 7.7 × 10^5, respectively. BP was purified by repeated recrystallization from ethanol solution. Spectroscopic grade benzene was used as a solvent. Irradiation of samples in quartz cells was carried out at 366 nm by using filtered light from a 500 W high-pressure mercury lamp. The flash photolysis apparatus was the same as that described by Yamamoto et al.[9] The flash excitation of samples was done with acetone-filtered light from a xenon-filled quartz flash lamp, operated at 8 kV and 3 μF. The pulse width of excitation light was about 18 μs. The molecular weights of the polymers were determined by viscometry. By GPC measurements, the polymers were shown to have most probable distributions before and after irradiation. In the present systems, therefore, we can assume that the ratio of the number-average molecular weights, $(M_0/M_t)_n$, is equal to the ratio of the viscosity-average molecular weights, $(M_0/M_t)_v$, where M_0 and M_t are the molecular weights of the polymers before and after an irradiation time of t, respectively. This relation was confirmed from the molecular weight measurements of the polymers by osmometry.

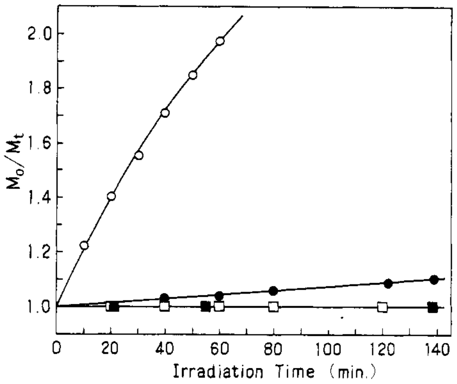

Figure 1. Photosensitized degradations of PSt (●, ■) and PMSt (○, □) by BP. [BP] = 0.5 × 10^{-2} M; [polymer] = 3.0 × 10^{-2} M (based on the monomer unit): (● and ○) under vacuum; (■ and □) in air.

The changes in the molecular weight of the polymers under various conditions are shown as a function of photoirradiation time in Figure 1. As is well known, the quantity of $(M_0/M_t) - 1$ is equal to the average number of chain scissions per original polymer molecule. The chain scission of PMSt occurs in vacuum much more rapidly than that of PSt, whereas no degradation of both polymers is observed in the presence of air.