Summary

Under some circumstances polymers in solutions can separate out into an isotropic phase at concentration c_I and a nematic phase at concentration c_N. In the presence of an elongational flow field, these concentrations change somewhat. We have derived a quasi-static thermodynamic theory connecting the change in the concentrations c_N and c_I to the applied strain rate. The formulas only include quantities which are, at any rate in principle, experimentally accessible. These quantities are the rate of change of osmotic pressure with respect to concentration in each phase, the partial molar volumes in each phase, the anisotropic part of the dynamic magnetic susceptibility in the nematic phase, and the quantity $(\partial H^2/\partial \dot{e})_{q=0}$, which is most easily determined experimentally by the ratio of the magnitude of the flow birefringence response to that of the Cotton–Mouton effect at the transition point (eq 44). The theory is analogous to the well-known Clausius–Clapeyron results. It is the differential form of the equation of state along a two-phase boundary. These results complement the statistical mechanical study of the same problem in ref 4.

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References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(2) Kramers, H. A. *J. Chem. Phys.* **1946**, *14*, 415.
(3) Bird, R. B.; Armstrong, R. C.; Hassager, O. "Dynamics of Polymeric Liquids"; Wiley: New York, 1977; Vol. I. Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, C. F. *Ibid.*, Vol. II.
(4) Marrucci, G.; Sarti, G. C. In "Ultra-High Modulus Polymers"; Giferri, A., Ward, I. M., Eds.; Applied Science Publishers: London, 1977.
(5) de Gennes, P. G. "The Physics of Liquid Crystals"; Oxford University Press: London, 1975.
(6) Beeby, J. L. *J. Phys. C* **1973**, *6*, 2262.
(7) See, for example: Landau, L. D.; Lifshitz, E. M. "Statistical Physics"; Pergamon Press: London, 1958; Chapter 8.
(8) Doi, M. *J. Phys. (Paris)* **1975**, *36*, 607. Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 540, 918. Auvray, L. *J. Phys. (Paris)* **1981**, *42*, 79.
(9) A discussion of magnetic birefringence (the Cotton–Mouton effect) is given in ref 5, pp 50–1. A discussion of flow birefringence occurs in ref 5, pp 211–2.

Triplet Energy Migration in Poly(acrylophenone): Dependence on Polymeric Tacticity

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ABSTRACT: Although the quantum yield of chain scission in poly(acrylophenone) (PAP) is about 0.40 and is independent of polymeric tacticity, the rates of other photoprocesses are not. Intramolecular quenching of the Norrish type II process by photoproducts is more efficient in i-PAP than in a-PAP. The reverse is true for intermolecular quenching of the carbonyl triplets by naphthalene in fluid solution at 30 °C. Stern–Volmer quenching constants are 70.1 and 15.2 M^{-1} in this case for the atactic and isotactic polymers, respectively. This difference is shown to arise as a result of the shorter triplet-state lifetime of the carbonyls in the isotactic polymer. For the atactic polymer an energy migration coefficient of 1.8×10^{-5} cm^2 s^{-1} was calculated, corresponding to a frequency of energy migration of 4.3×10^{10} s^{-1}. The root-mean-square migration length of 90 Å is less than the estimated coil dimension of about 200 Å. The quenching of phosphorescence intensity in 77 K solid solutions was found to be well described by the Perrin model. Active spheres of quenching were calculated to be 22.5 and 20.3 Å for the isotactic and atactic polymers, respectively.

Introduction

The photochemistry of poly(acrylophenone), also referred to as poly(phenyl vinyl ketone), has been extensively studied in the past decade. This polymer represents a particularly good model to determine the differences to be expected between small-molecule and macromolecular ketones containing a regularly recurring sequence of chromophores. Because of rapid intersystem crossing from the first excited singlet to the triplet, most of the observed photoprocesses can be considered as arising from the latter state, thus simplifying the interpretation of experimental results.

It has recently become apparent that the stereoregularity of a polymer chain can significantly affect the photoprocesses undergone by chromophores attached to it. For example, excimer formation has been shown[1-5] to be more efficient in isotactic polystyrene than in its atactic analogue, both in fluid solutions and in 77 K solid matrices. Tanaka and Otsu[6] have reported that poly(*tert*-butyl vinyl ketone) undergoes photodegradation more readily in the atactic than in the isotactic form. However, Kilp et al.[7] have shown that the quantum yield of the main-chain scission in poly(acrylophenone) is of the order of 0.40 and is independent of tacticity. In view of the differences which have been cited above, it was felt that a further investigation of the photoprocesses involved would prove to be of interest.

Experimental Section

Details of polymer synthesis and degradation techniques have previously been described.[7] Inhibition of chain scission was accomplished by the addition of naphthalene (purified by vacuum sublimation) to the polymer solutions.

The solvent used to form low-temperature glasses was in all cases α-methyltetrahydrofuran (α-MTHF) from Matheson

Table I
Molecular Weights and UV Absorptions of PAP Homopolymers

			UV absorption,[b,c] nm	
polymer	$\bar{M}_n$[a]	^1L_a	^1L_b	n → π*
i-PAP-1	274 000	244 (4.11)[d]	280 (3.13)	325 (1.89)
i-PAP-2	470 000	244 (4.03)	280 (3.12)	325 (1.87)
a-PAP-1	70 000	244 (4.12)	280 (3.13)	325 (1.89)
a-PAP-2	360 000	244 (4.13)	280 (3.15)	325 (1.90)
isobutyrophenone				323 (1.79)

[a] From membrane osmometry in toluene solution. [b] In methyltetrahydrofuran solution. [c] Absorption bands named using Platt notation. [d] Value in parentheses is log ε.

Coleman and Bell. It was purified by refluxing over cuprous chloride for 3 h followed by distillation under a nitrogen atmosphere. No impurities were detectable in the absorption, emission, or excitation spectra of the solvent. It was stored in a brown glass bottle under a blanket of nitrogen in order to inhibit impurity formation. Only freshly distilled solvent was used to make up solutions for emission studies. Any solution that was more than 2 or 3 days old was discarded and a fresh one was prepared for further work. Emission measurements were made on polymer solutions that were (1–3 × 10^{-3} M in ketone units. Excellent, clear glasses were obtained at 77 K.

Emission spectra were obtained with either a Perkin-Elmer Model MPF-2A fluorescence spectrometer or a Spex Fluorolog Model 1902 single-photon-counting fluorescence spectrometer. The coolant in all cases was liquid nitrogen.

All spectra were recorded with 90° viewing of emission. No corrections for photomultiplier response or diffraction grating effects were applied. Relative emission intensities were derived from the total areas under the spectra as measured by an Ott planimeter.

Laser flash photolysis experiments were carried out with an apparatus previously described by Encinas and Scaiano.[8] Excitation of the samples was accomplished with the pulses (337.1 nm, ~8 ns, 3 mJ) from a Molectron UV-400 nitrogen laser. Transient absorbances were monitored by using a pulsed Eimac 150-W xenon lamp, the output of which was initially focused onto the sample area irradiated by the laser and subsequently onto the entrance slit of a Bausch & Lomb high-intensity monochromator. Variations in the intensity of the probe beam were then monitored with an RCA-4840 photomultiplier tube with four dynodes connected. The signals were terminated into 93 Ω and into a Tektronix R7912 transient digitizer. The data were then transmitted to a PDP 11/55 multiuser computer system which, as well as controlling the experiment itself, performed any required signal averaging, data processing, and long-term storage of acquired results.

Distributions and polydispersities of the polymers were determined with a Waters Associates Model 200 Ana-Prep gel permeation chromatograph (GPC) using Bioglass columns. Seven columns were used in series, having pore sizes of 2500, 1500, 1000, 500, 200, 125, and 75 Å. The working solvent was toluene.

As aromatic ketones absorb light of wavelength greater than 300 nm quite efficiently, all polymer synthesis, solution preparations, and subsequent measurements were carried out in a darkened room. This eliminated the possibility of photoproduct formation due to absorption of the output from the fluorescent room lighting.

Results and Discussion

Polymer Characterization. Two samples each of isotactic and atactic poly(acrylophenone), PAP, were used. Their molecular weights and characteristic ultraviolet absorption bands are listed in Table I. The absorption of the small molecule isobutyrophenone, which can be considered to be a model for the system, is also indicated.

The four polymers all exhibit a low-intensity band with its maximum at 325 nm (log ε ≈ 1.89) in MTHF solution. A shift to slightly longer wavelengths (λ_{max} 327 nm, log ε = 1.94) in going to the less polar solvent benzene is typical of an n → π* transition.

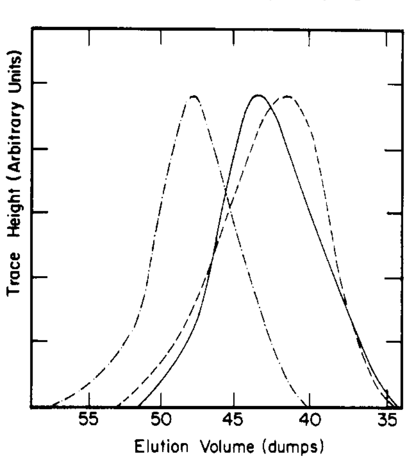

Figure 1. Molecular weight distributions of PAP homopolymers: (——) i-PAP-2; (– – –) a-PAP-2; (–·–) a-PAP-1.

It is interesting that the small molecule isobutyrophenone shows a weaker absorption at a slightly shorter wavelength (λ_{max} 323 nm, log ε = 1.79) than do the PAP polymers in MTHF solution. This shift in UV absorption has been previously noted by Somersall and Guillet[9] in the case of small-molecule and polymeric aliphatic ketones.

Molecular weight distributions as determined by GPC are shown in Figure 1. Attempts to numerically evaluate their polydispersities through the use of the universal calibration technique[10] were unsuccessful. Although automatic viscometry enabled us to measure quite accurately the increase in efflux time due to the small amount of polymer in the fractions collected from the leading and trailing edges of the chromatograms, large errors were involved in the calculation of the concentrations of these aliquots. Since the value of the polydispersity is strongly dependent upon the analysis of these regions of the chromatogram, the results which were obtained were considered unreliable.

Nonetheless, Figure 1 does show that the distribution of i-PAP-2 is slightly skewed toward low molecular weight species while the opposite is true of a-PAP-2. From the peak widths at half-maximum it can be inferred that the isotactic polymer has a slightly narrower distribution than does the atactic polymer.

Even though i-PAP-2 has a number-average molecular weight higher than that of a-PAP-2 (470 000 vs. 360 000), it must have a smaller hydrodynamic volume than that of the atactic polymer. This can be seen from the higher elution volumes required to record its chromatogram.

Energy Migration in Fluid Solutions. Irradiation by light of 313- or 364-nm wavelength results in the exclusive excitation of the carbonyl chromophore in the polymer side chains. This excitation energy may be dissipated in several ways, one of which is the classic Norrish type II photochemical reaction, resulting in main-chain scission, hence reducing its molecular weight. The reaction can be conveniently followed by the technique of automatic viscometry.[11] The results of the 313-nm irradiation of a-PAP-1 and i-PAP-1 in benzene solutions at 30 °C are shown in Figure 2.

While the initial quantum yields of chain scission appear to be independent of tacticity for the PAP polymers studied, it can be seen from Figure 2 that plots of chain scission vs. irradiation time are nonlinear. Theoretical calculations[12,13] of the extent of random degradation as a function of equal increments of absorbed irradiation predict a linear relationship between (molecular weight)$^{-1}$ and

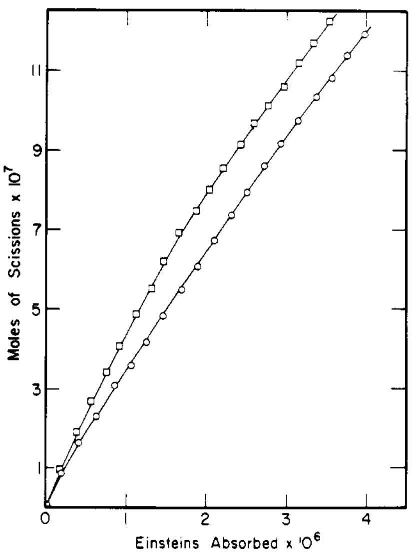

Figure 2. Photolysis of PAP homopolymers in benzene solutions (7.58×10^{-3} M in ketone units), 30 °C, 313 nm: (□) a-PAP-1; (○) i-PAP-1.

exposure time. Experimentally, however, curvature is almost always observed. In the initial stages of degradation (up to 1.5×10^{-6} einstein absorbed) this curvature is greater for the isotactic polymer.

The Norrish type II split in polyketones produces a chain-end ketone and a chain-end olefin. It is probable that the latter is capable of acting as a quencher of other electronically excited carbonyls. Decreases in the quantum yield of the type II process in small-molecule aromatic ketones have been attributed by Wagner et al.[14] to the buildup of photoproducts capable of acting as quenchers.

Quenching by the chain-end olefin photoproduct may be either intra- or intermolecular. However, since the concentration of the polymer solutions irradiated was only 7.58×10^{-3} base moles liter^{-1}, the former mechanism is much more likely. Intramolecular quenching can occur by either of two processes, energy migration down the polymer chain followed by trapping by the chain-end quencher or by a collisional process involving the diffusion of the chain end in solution. The extent to which these processes occur appears to be dependent upon polymer tacticity as evidenced by the greater curvature in the isotactic polymer.

It is interesting to construct Stern–Volmer quenching plots from the initial data points in Figure 2. The number of main-chain breaks as a function of irradiation time is known from viscometric measurements. Since each scission produces one chain-end olefin, it is possible to calculate the overall concentration of quencher at each stage of the degradation. The slope of the line connecting the first two data points (including the origin) in Figure 2 is taken as the unquenched quantum yield, ϕ_0. The quenched values, ϕ_Q, are then obtained from the slopes of the lines connecting each subsequent pair of data points. Results of this procedure are shown in Figure 3.

It can be seen that for the initial stages of degradation where the extent of curvature is greatest, acceptable Stern–Volmer quenching plots are obtained. Values of the Stern–Volmer quenching constants, K_{SV}, are 6.1×10^4 and 10.6×10^4 M^{-1} for a-PAP-1 and i-PAP-1, respectively. These large values are similar to those of Lukac et al.,[15] who reported that inhibition of chain scission in poly(acrylophenone) by naphthalene is some 20 times more efficient when the quencher is present in the polymer chain as vinylnaphthalene rather than as a freely diffusing additive in the solution. However, as has been pointed out by George,[16] correction for the much higher "effective concentration" of the quencher in the neighborhood of the polymeric carbonyls when it is bound to the chain would substantially reduce the values of K_{SV}. We can therefore only use the results of Figure 3 for a qualitative comparison between the behavior of the atactic and isotactic polymers.

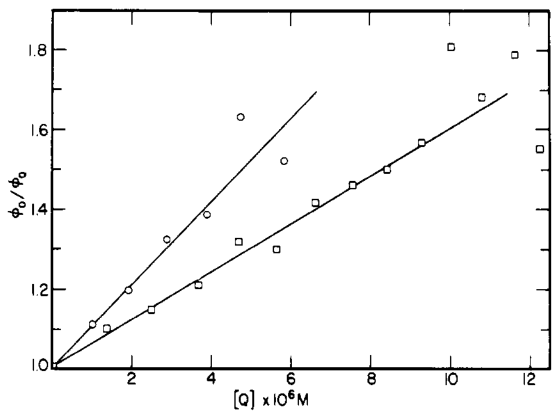

Figure 3. Stern–Volmer plots of intramolecular inhibition of chain scission by photoproducts: (□) a-PAP-1; (○) i-PAP-1.

Since isotactic PAP undergoes intramolecular quenching to a greater extent than the atactic polymer, the contributions due to energy migration and chain-end diffusion may well differ and be dependent upon the preferred conformations of the two polymers in solution. Although these are not known with certainty, it seems likely that the isotactic polymer might have a high degree of helical content while the atactic polymer exists as a random coil.

D'Alagni et al.[17] have attributed differences in the far-UV spectra of isotactic and syndiotactic poly(methyl methacrylate) to the fact that the isotactic polymer exists in solution largely as a 5/1 or 5/2 helix, the former being characterized by a much closer approach between the ester functionalities. Pino et al.,[18] in studying the optical activity of poly(α-olefins), have postulated that agreement between experimentally observed and calculated values of optical rotation of very stereoregular polymers arises from the fact that these polymers are largely helical, not only in the solid state but also in solution at room temperature. Natta[19] has shown that isotactic polystyrene possesses a 3/1 helical conformation identical with that observed in its crystalline state. Helical sequences are also found in the atactic polymer but they are fewer and of shorter range than those in the isotactic case.

Our GPC results also support this assumption. It was noted that i-PAP-2 appeared at elution volumes significantly larger than those for a-PAP-2 even though it possessed a considerably higher molecular weight. Furthermore, despite the large difference in $\bar{M}_n$ values, the intrinsic viscosities of undegraded i-PAP-2 and a-PAP-2 are almost identical, being 0.810 and 0.783 dL/g, respectively. Although, strictly speaking, intrinsic viscosity varies as a function of $\bar{M}_v$, the viscosity-average molecular weight, the relatively low polydispersities of the two polymers allows a comparison to be drawn on the basis of $\bar{M}_n$. These two results, then, can only be rationalized on the basis of a lower hydrodynamic volume for the isotactic polymer. In order to achieve this despite a larger molecular weight, the isotactic chain must exhibit a tighter packing in solution. This is most likely to be accomplished by the assumption of a helical configuration.

It is interesting to note that despite the apparent differences in their solution conformations, the Mark–Houwink parameters of the two polymers are independent of tacticity.[7] Danusso and Moraglio[20] have reported that

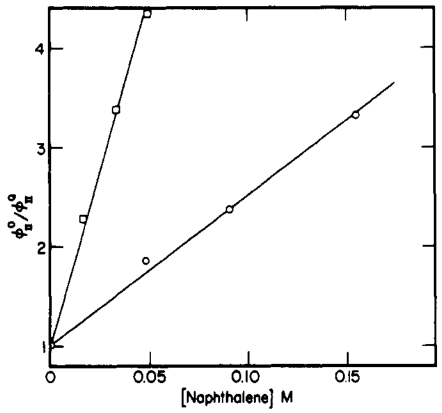

Figure 4. Inhibition of chain scission by naphthalene: (□) a-PAP-2; (○) i-PAP-2. All conversions to a maximum of one scission per chain.

while isotactic and atactic polystyrene yield identical K and a values, their second virial coefficients are dependent upon polymeric stereoregularity. If these quantities are taken as a reflection of the extent of polymer–polymer and polymer–solvent interactions, then it can be seen that tacticity clearly affects the solution configuration of the chains. In this case, inferences drawn from a comparison of the magnitudes of K and a would in all probability be invalid as the chains would not exist in the required randomly coiled configuration.

If differences in solution conformation exist, then the rate of other observable photophysical processes may also depend on tacticity.

The inhibition of chain scission by naphthalene is shown plotted in Stern–Volmer form in Figure 4, where $\phi_{II}{}^0$ and $\phi_{II}{}^Q$ refer to quantum yields in the absence and the presence of Q, respectively. A large difference is readily apparent. In contrast to the intramolecular case, intermolecular quenching of the chain-scission reaction is markedly more efficient in the atactic polymer. Values of the Stern–Volmer quenching constants, K_{SV}, are 70.1 and 15.2 M^{-1} for a-PAP-2 and i-PAP-2, respectively.

The value of K_{SV} (70.1 M^{-1}) for the atactic polymer corresponds very well with the value of 68 M^{-1} reported by Lukac et al.[15] for inhibition by the same quencher in benzene solution at 30 °C. A somewhat higher value of 82 M^{-1} has found by Faure et al.[21] when methylnaphthalene is used as the quencher.

The dependence of tacticity of the efficiency of naphthalene in quenching chain scissions might be explained by coil penetration effects as discussed by Oster and Nishijima.[22] If, as our previous results would indicate, i-PAP exists as a more tightly packed coil in solution, then it might be more difficult for naphthalene to diffuse into it. Excited chromophores located in the interior of an i-PAP coil would then not be quenched as efficiently as those similarly situated in a-PAP. The difference in K_{SV} values as noted above would then be observed.

Ishii et al.[4] have reported similar tacticity effects in their studies of polystyrene. The quenching of monomer fluorescence in fluid solution by carbon tetrachloride was found to be more efficient in the atactic as compared to the isotactic polymer, K_{SV} values being 13.5 and 8.7 M^{-1}, respectively. Excimer formation, which reduces the lifetime of the excited state, was found to occur at a higher rate and with a lower activation energy in the isotactic polymer. Therefore, the differences in quenching efficiency were attributed to the shorter excited-state lifetime of the monomer in an isotactic chain. Our values of K_{SV} might also be explained by a shorter excited-state lifetime, τ_3, of the carbonyls in i-PAP. Laser flash photolysis experiments were therefore carried out to examine this possibility.

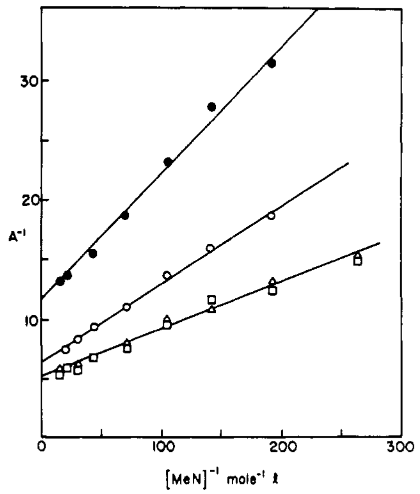

Figure 5. Sensitization of 1-methylnaphthalene triplets: (□) a-PAP-2; (△) a-PAP-1; (○) i-PAP-2; (●) i-PAP-2 (deaerated).

Direct determination of carbonyl τ_3 values is complicated by the overlap of the transient absorptions of both the triplet ketone and the biradical species. Furthermore, the pulse width of the Molectron UV-400 nitrogen laser was too long to permit reliable estimates of τ_3 to be made in the absence of deconvolution of the measured decays. Triplet lifetimes were therefore determined by using the 1-methylnaphthalene (MeN) quencher technique described by Bays et al.[23]

Excitation of the carbonyl chromophores in the presence of MeN results in the formation of triplet-state acceptor via energy transfer. The latter is much longer-lived than is the carbonyl triplet and exhibits a strong transient absorbance at 415 nm. If the absorbance A_{MeN} of the triplet MeN immediately following the laser pulse is measured as a function of the overall quencher concentration, Bays et al.[23] have shown that the value of $k_q\tau_3$ can be determined from

$$A_{MeN}{}^{-1} = \alpha + \alpha(k_q\tau_3[MeN])^{-1} \qquad (1)$$

The quantity α is a constant given by

$$\alpha = (\phi_{ISC}I_0\epsilon l)^{-1} \qquad (2)$$

where ϕ_{ISC} is the quantum yield of intersystem crossing for the ketone, I_0 is the absorbed light intensity from the laser pulse, ϵ is the extinction coefficient of triplet MeN, and l is the optical path length in the sample cell. In practice, the magnitude of α need not be explicitly determined as values of $k_q\tau_3$ are obtained from the intercept to slope ratio of data plotted according to eq 1.

Figure 5 shows the results of the triplet MeN sensitization studies in benzene solutions using polymeric donors, plotted according to eq 1. Since exact reproducibility in the overlap between exciting and monitoring beams as well as in the laser pulse power is not possible on a day-to-day basis, intercept values are variable. Table II lists the results of these studies as well as the K_{SV} values previously determined by naphthalene inhibition of chain scission. Also listed are the results from an acetophenone–MeN experiment. In this case the carbonyl triplet lifetime was directly determined by the decay of its transient absorbance at 380 nm in an aerated benzene solution in the absence of MeN quencher. This lifetime (135 ns) was then used to calculate the k_q value of 4.8 × 10^{-9} M^{-1} s^{-1}. With

Table II
Quenching of the Carbonyl Triplet States

sample	K_{SV},[a] M^{-1}	$k_q\tau_3$,[b] M^{-1}	$k_q \times 10^{-9}$, $M^{-1}\ s^{-1}$	τ_3,[c] ns
i-PAP-2[d]	15.2	109.2	2.4[e]	46
i-PAP-2		98.4	2.4[e]	41
a-PAP-2	70.1[d]	131.9	2.4[e]	55
acetophenone		652.5	4.8	135[f]

[a] From quenching of chain scission using naphthalene. [b] From sensitization of MeN triplet. [c] Triplet ketone lifetime. [d] Deaerated solutions. [e] From ref 23. [f] From direct measurements of decay of triplet ketone absorbance.

the exception of one i-PAP sample, all results were determined by using aerated solutions.

The polymeric ketone triplet lifetimes listed in Table II were calculated from the measured $k_q\tau_3$ values using $k_q = 2.4 \times 10^9\ M^{-1}\ s^{-1}$. This quenching constant was obtained by Bays et al.[23] using a low ketone content poly(methyl methacrylate-*co*-acrylophenone) copolymer in which a direct measurement of τ_3 was possible due to a lack of γ hydrogens.

For i-PAP-2, purging the solution with argon marginally increased the triplet carbonyl lifetime from 41 to 46 ns. The aerated samples of a-PAP-1 and a-PAP-2 yielded identical τ_3 values of 55 ns, clearly greater than the 41 ns measured for the isotactic polymer under similar conditions. It should be emphasized here that these τ_3 values only represent upper limits of the actual triplet lifetimes. The k_q value used in these calculations was measured[23] for a polymer in which triplet energy migration is relatively unimportant. Energy migration in the homopolymers[23] may well increase k_q by a factor of 2–3, thereby reducing the τ_3 values correspondingly. Further, if intramolecular energy migration is more facile in the isotactic than in the atactic polymers as suggested above, the disparity in their τ_3 values would be even greater than that shown in Table II. Increasing stereoregularity in the PAP homopolymers therefore clearly results in decreasing carbonyl triplet lifetimes.

In the absence of bimolecular quenching, the triplet state in the ketone chromophore in fluid solution is depleted by three major processes: intersystem crossing back to the ground-state singlet (a radiationless process), self-quenching, and hydrogen abstraction. An increase in one or all of these rates in i-PAP is required to produce a shorter triplet lifetime.

Changes of any significance in the rates of intersystem crossing back to ground-state singlet are difficult to rationalize on the basis of polymer configuration. An increase in the extent of self-quenching in the isotactic polymer is quite likely on the basis of our arguments with respect to coil conformation in solution. However, acetophenone[24,25] and benzophenone[26,27] undergo self-quenching with rate constants k_{SQ} on the order of $10^6\ M^{-1}\ s^{-1}$, while Lewis[28,29] has shown that the rate constant for radiationless decay, k_{ISC}, from the triplet state is less than $10^6\ s^{-1}$ for small-molecule alkyl aryl ketones in benzene solution.

In order to compete effectively with known rates[30] of γ-hydrogen abstraction in a-PAP ($10^7\ s^{-1}$ or higher) for the depletion of the triplet excited states, very large increases in one or both of k_{SQ} or k_{ISC} would be required. That this does not occur is shown by the invariance of the quantum yield of chain scission, ϕ_{II}, with tacticity. Large changes in either k_{ISC} or k_{SQ} would affect the extent of 1,4-biradical formation, resulting in differences in the measured values of ϕ_{II}. Since this is not observed, the differences in triplet lifetimes cannot be explained in terms of either self-quenching or intersystem crossing rates.

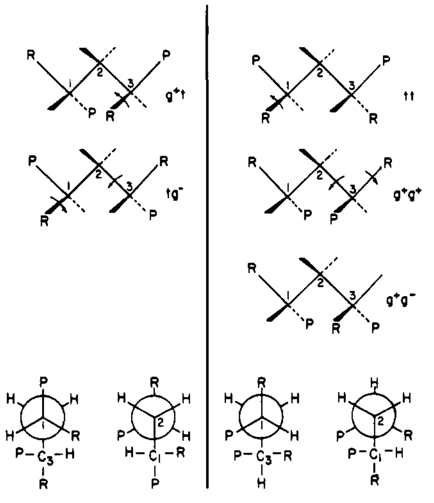

Figure 6. Local conformations in isotactic and atactic PAP.

On the other hand, if γ-hydrogen abstraction occurs at a higher rate in i-PAP than in a-PAP, its triplet lifetime would be decreased but $\phi_{II}{}^0$ values would remain identical. In the absence of bimolecular quenching, γ-hydrogen abstraction is the major mode of deactivation in both polymers. Hence while the *rate* of 1,4-biradical formation may be larger and result in shorter τ_3 values in i-PAP, the *extent* of biradical formation remains the same in both polymers. Since the experimentally measured values of chain-scission quantum yield reflect the behavior of the 1,4-biradical and this is identical for both a-PAP and i-PAP,[7] $\phi_{II}{}^0$ remains independent of tacticity.

If the rate of γ-hydrogen abstraction in i-PAP is significantly higher than in a-PAP, it must arise as a result of differing conformational effects on the ability of each to form the six-membered-ring cyclic intermediate required by the type II process. Inductive effects and γ-hydrogen bond strengths due to substitution on the γ carbon are clearly identical.

Shimanouchi et al.[31] have determined the preferential conformations of racemic (*dl*) and meso (*dd*) 2,4-dichloropentanes in solution to be tt $\rightleftarrows$ g^+g^+ and $g^+t \rightleftarrows tg^-$, respectively. Bovey et al.[32] have confirmed these structures for the isomers of 2,4-diphenylpentane by NMR studies over a wide range of temperatures.

The racemic and meso isomers of these compounds can be taken as models of atactic and isotactic PAP, respectively, in the consideration of their local conformations. Figure 6 illustrates the probable polymeric low-energy states by application of the results of the small-molecule studies to them. P denotes the polymer chain and R represents the benzoyl group. It has been shown by Merle-Aubry[33] by ^1H NMR studies of the *meso*-2,4-dibenzoylpentane model dimer that the local preferential conformation of i-PAP is $g^-t \rightleftarrows tg^+$, thus substantiating the structures in Figure 6.

It can be seen that in the g^+t and tg^- conformations of i-PAP and the tt conformation of a-PAP, only rotation about a C–R bond is required to reach the cyclic intermediate preceding hydrogen abstraction.

From the g^+g^+ state of a-PAP, rotations about C_3–R and C_2–C_3 are required to reach a conformation propitious to γ-hydrogen abstraction denoted by g^+g^-. The Newman projections along C_1–C_2 and C_2–C_3 for the latter state are also shown in Figure 6. It is clear that steric interactions between substituents on C_2 and C_3 would be highly unfavorable in the g^+g^- conformation of a-PAP. This can be contrasted to the tg^- conformer of the isotactic polymer, whose Newman projection is also shown. Therefore, γ-hydrogen abstraction must occur predominantly from the tt low-energy conformer in the atactic polymer. In contrast to this, in i-PAP, hydrogen abstraction can proceed equally well from both the g^+t- and tg^--state precursors. In this case the triplet lifetime of the aromatic carbonyl of i-PAP will be shortened as listed in Table II and quenching of chain scissions by added naphthalene would be less effective as shown in Figure 4.

If either the rate of quenching, k_q, or the unquenched triplet lifetime, τ_3, is known from an independent measurement, then the other quantity is calculable from the measured K_{SV} values listed in Table II. Faure et al.[21] have reported a τ_3 value of 7.5×10^{-9} s for a-PAP in benzene solution at 30 °C. Assuming that the triplet lifetime is not greatly affected on going to a toluene solution at 30 °C, a quenching rate constant k_q of 9.35×10^9 M^{-1} s^{-1} can be calculated from our K_{SV} value of 70.1 M^{-1} for a-PAP-2. Faure's value of τ_3 was obtained by direct observation of the decay of the transient absorbance of the triplet carbonyl. It is therefore preferred here over those τ_3 values listed in Table II, which, as has been pointed out, can only be considered upper limits of the actual lifetime.

The diffusion-controlled rate of quenching may be calculated from the Smoluchowski equation as modified by Ware and Novros[34] and Yguerabidi et al.:[35]

$$k_{\mathrm{diff}} = \frac{4\pi r D N}{1000}\left[1 + \frac{r}{(D\tau_0)^{1/2}}\right] \qquad (3)$$

where r and D are the sums of donor and acceptor collisional radii and diffusion coefficients, respectively, N is Avogadro's number, and τ_0 is the unquenched donor lifetime. The assumption that is commonly made in the application of eq 3 is that the collisional radii are identical in acceptor and donor, i.e., that $r_A = r_D$. This implies that the quencher can be considered to be interacting only with the excited carbonyl group and not the entire macromolecule. Furthermore, Heskins and Guillet[36] have suggested that the diffusion of the center of mass of the polymer coil in solution is negligible in comparison to that of the small-molecule quencher. This is supported by the values in Table II, which show that k_q for the acetophenone–MeN system is twice as large as that for the polymer–MeN system studied by Bays et al.[23] Therefore only the diffusion coefficient of the quencher naphthalene enters into eq 3.

The magnitude of the collisional radius is often evaluated from

$$r_A = (V_1/N)^{1/3}/2 \qquad (4)$$

where V_1 is the LeBas molar volume and N is Avogadro's number. V_1 is defined as the volume containing N spherical molecules packed in an orderly cubic array. Gorrel and Dubois[37] have calculated an r_A value of 3.1×10^{-8} cm for naphthalene.

If r_A is known, the diffusion coefficient, D_A, can be calculated from the Stokes–Einstein equation:

$$D_A = RT/6\pi\eta r_A \qquad (5)$$

where R is the gas constant and T is the temperature. As Heskins and Guillet[36] have shown, the viscosity, η, of pure solvent should be used in eq 5 rather than the macroscopic viscosity of the solution. One therefore considers the microviscosity of the medium which the quencher diffuses through as being equal to that of pure solvent. This is supported by the results of Weyl,[38] who found that the addition of polystyrene to solutions of pyrene did not affect the diffusion-controlled photophysical processes that the latter typically undergoes.

Using values of 3.1×10^{-8} cm and 5.26×10^{-3} P for r_A, the collisional radius of naphthalene, and the viscosity of toluene at 30 °C, respectively, we obtain from eq 5 a value of 1.36×10^{-5} cm^2 s^{-1} for D_A, the diffusion coefficient of naphthalene.

With the usual approximations that $r = 2r_A$, $D = D_A$, and $\tau_0 = 7.5 \times 10^{-9}$ s, we can calculate from eq 3 a value of 7.62×10^9 M^{-1} s^{-1} for k_{diff}. This is smaller than the value of 9.35×10^9 M^{-1} s^{-1} for k_q as determined from our K_{SV} values.

If we define an efficiency of energy transfer α as the ratio k_q/k_{diff}, an apparent value of 1.2 is obtained. This may be compared to values of α less than unity as reported by Wagner and Kochevar[39] for quenching of small-molecular alkyl aryl ketones in low-viscosity solutions. Similarly, a value of 0.52 for α has been reported by Takemura et al.[40] for the quenching of triplet acetophenone by naphthalene in isooctane ($\eta = 0.51$ cP) at 25 °C. The inefficiency of energy transfer in these cases can be attributed to short encounter times due to a small solvent cage effect. This allows the separation by diffusion of the encounter complex formed by the excited donor and acceptor before energy transfer can occur.

The increased efficiency of transfer in the polymeric case may well be due to intramolecular energy migration. In this case a kinetic model developed by Voltz et al.[41] is applicable. Voltz modified the Smoluchowski equation as shown in eq 3 to include the possibility of an energy migrational term assuming some importance. The result is a rate constant k'_{diff} which now reflects a collision rate arising from both diffusion and energy migration:

$$k'_{\mathrm{diff}} = \frac{4\pi r N(D + \Lambda)}{1000}\left[1 + \frac{r}{[(D + \Lambda)\tau_0]^{1/2}}\right] \qquad (6)$$

where D represents the sum of the diffusion coefficients as before and Λ is the energy migration coefficient.

The value of k'_{diff} can be determined as k_q/α if the true value of α is known. Faure et al.[42] in a similar calculation on the quenching of a-PAP by methylnaphthalene have used a value of 0.56 for α. This was their magnitude of the quenching efficiency constant measured for the valerophenone–methylnaphthalene system in benzene at 30 °C. Our use of the same value can be justified by the seeming invariance of α for aromatic ketone–naphthalene systems as evidenced by the results of Takemura.

Substitution into eq 6 yields a value of 3.16×10^{-5} cm^2 s^{-1} for $D + \Lambda$. Since D is taken as the diffusion coefficient of naphthalene alone (1.36×10^{-5} cm^2 s^{-1}), a value of 1.80×10^{-5} cm^2 s^{-1} is obtained for the energy migration coefficient.

The frequency of energy migration may be calculated from

$$w = 6\Lambda/r^2 \qquad (7)$$

where r is the separation between the carbonyl chromophores. If this is taken to be 5 Å,[42] then a value of 4.3×10^{10} s^{-1} is obtained for the frequency of energy migration, w. This compares very well with the values of 5×10^{10} s^{-1} reported by Faure et al.[42] and 3×10^{10} s^{-1} reported by Bays et al.[23] from the quenching of a-PAP triplets by methylnaphthalene in benzene solutions.

In the absence of an independently determined value of the triplet lifetime, a similar calculation cannot be carriet out for the isotactic polymer.

David et al.[43,44] have found a value of 7×10^4 s^{-1} for w in poly(vinylbenzophenone) films at 77 K and 128 s^{-1} for poly(vinylnaphthalene) in glassy solutions at the same temperature. A value of 300 s^{-1} in poly(naphthyl methacrylate) films at 77 K has been reported by Somersall and Guillet.[45] Thus our calculated value of w is considerably higher than results obtained from polymers whose large-scale molecular motions are frozen out by virtue of their incorporation into films or glassy solutions at 77 K.

It is interesting that the frequency of energy migration in benzophenone crystals containing trace amounts of naphthalene was found to be 10^{10} s^{-1} by David et al.[46] This is very similar to our result. This might be taken to imply that in fluid solution, more so than in 77 K films or solid solutions, the polymeric chromophores are already in orientations favorable for triplet energy migration (or, conversely, that migration does not require rigid orientation of the chromophores).

If we describe the migration of the energy along the chain as a random walk, then the root-mean-square migration length, r_m, is given by

$$r_m = (2\Lambda\Delta\tau)^{1/2} \tag{8}$$

$$r_m = (6\Lambda\Delta\tau)^{1/2} \tag{9}$$

for a walk in one and three dimensions, respectively, and $\Delta\tau$ is the excited-state lifetime. It is not yet completely clear which model is most applicable to energy migration in polymers. When the energy is confined to a single chain, it may be viewed in a first approximation as undergoing a random walk in a one-dimensional crystal. Equation 8 would then be applicable. However, as has been pointed out by Powell,[47] even though the excitation may remain on a single chain, the chain itself wanders in three dimensions. Therefore the excitation can approach the quencher from any direction in three dimensions and eq 9 should be used.

Substituting 1.80×10^{-5} cm^2 s^{-1} and 7.5×10^{-9} s for Λ and $\Delta\tau$, respectively, into eq 9 results in a root-mean-square migration length r_m of 90 Å.

According to the theory of Flory,[48] the intrinsic viscosity of a polymer solution is given by

$$[\eta] = 6^{3/2}\Phi(\langle \bar{S}^2 \rangle)^{3/2}/\bar{M}_n \tag{10}$$

where Φ is a universal constant (2.1×10^{21}), $\langle \bar{S}^2 \rangle$ is the mean-square radius of gyration, and $\bar{M}_n$ is the molecular weight. Substituting the values 0.783 and 360 000 for $[\eta]$ and $\bar{M}_n$, respectively, a value of about 200 Å is found for the coil dimension of a-PAP-2 in toluene solution at 30 °C. Comparison with the root-mean-square migration length of 90 Å leads to the conclusion that a considerable portion of the polymer chain is visited by the migrating excitation during its lifetime.

It should be pointed out that much of the above may be somewhat fortuitous. The frequencies of energy migration in the various polymers mentioned have all been calculated by using some form of the Voltz model. Birks and Leite[49] have found considerable discrepancies between experimental data and predictions based on this model. They attributed the differences to an incorrect assumption of the boundary conditions determining the probabilities of energy transfer. While the absolute values of Λ and w calculated on this basis may be unreliable, comparisons based on their relative magnitudes should still be valid. As a result, the Voltz model is still widely applied at present.

Energy Migration in Solid Solutions. Further investigations of polymeric aromatic carbonyls can be carried out by the observation of their photoemissive behavior. Since the phosphorescence intensities of these systems are negligible in room-temperature solutions (as a result of deactivation of excited states by rapid γ-hydrogen abstraction), low-temperature glasses are needed when using conventional, low-intensity light sources to probe their photophysical processes.

In polymeric systems, one also encounters solubility problems. The number of solvents which form clear glasses at 77 K and still allow dissolution of the polymers is very small. This makes it difficult to study the effects of changing solvent polarity and rigidity. We have found that α-methyltetrahydrofuran is an excellent solvent and gives clear glasses at 77 K.

The phosphorescence emission spectra of the isotactic (i-PAP-2) and atactic (a-PAP-1, a-PAP-2) poly(acrylophenones) were virtually identical. The spectrum obtained with 340-nm excitation into the ketone n,π* singlet and right-angle viewing consisted of a series of vibronic bands. The 0–0, 1–0, and 2–0 transitions were clearly visible at 396 (25 252 cm^{-1}), 424 (23 584 cm^{-1}), and 456 (21 930 cm^{-1}) nm, respectively. Their spacing is fairly consistent at 1660 cm^{-1} and corresponds well with the infrared carbonyl stretching frequency at 1675 cm^{-1}. Excitation spectra of all three polymers were also identical and invariant with the wavelength of observation.

The quenching of phosphorescence was accomplished by the addition of naphthalene to the polymeric solutions. The latter is well-known as an effective quencher of aryl alkyl ketone triplets and is not directly excited by the 340-nm radiation that was used. No sensitized phosphorescence of naphthalene was detected at the instrumental sensitivities used when a rotating-cam attachment on the phosphoroscope was employed to separate long- and short-lived emissions.

The quenching of phosphorescence emission in aromatic ketones can be described by the following scheme, where D and A refer to donor and acceptor, respectively:

$$\mathrm{D} + h\nu \rightarrow \mathrm{D_3}^* \tag{11}$$

$$\left.\begin{aligned} &\mathrm{D_3}^* \rightarrow \mathrm{D} + h\nu \qquad k_\mathrm{R} \quad (12) \\ &\mathrm{D_3}^* \rightarrow \mathrm{D} \qquad\quad\;\; k_\mathrm{NR} \quad (13) \end{aligned}\right\} k_\mathrm{T}$$

$$\mathrm{D_3}^* + \mathrm{D} \rightarrow \mathrm{D} + \mathrm{D_3}^* \qquad k_\mathrm{mig} \tag{14}$$

$$\mathrm{D_3}^* + \mathrm{A} \rightarrow \mathrm{D} + \mathrm{A_3}^* \qquad k_\mathrm{AT} \tag{15}$$

Equation 11 represents excitation into the first singlet state of D followed by rapid intersystem crossing to the first triplet state. The other processes represented by eq 12–15 are radiative and nonradiative deactivation, energy migration, and energy transfer, the rates of which are given by k_R, r_NR, k_mig, and k_AT, respectively.

An analysis of this scheme using the stationary-state approximation for the concentration of the excited states gives

$$\begin{aligned} I_0/I &= 1 + (k_\mathrm{AT}/k_\mathrm{T})[\mathrm{A}] \\ &= 1 + k_\mathrm{AT}\tau_0[\mathrm{A}] \end{aligned} \tag{16}$$

where I_0 and I are the intensities of emission from $\mathrm{D_3}^*$ in the absence and the presence of the acceptor, respectively, and τ_0 is the unquenched triplet lifetime.

This is a form of the well-known Stern–Volmer equation and has been successfully applied by David et al.[50,51] to studies of energy transfer and migration in films and glassy solutions of poly(styrene-*co*-vinylbenzophenone) and by Somersall and Guillet[45] for the phosphorescence quenching of poly(naphthyl methacrylate) in solid solution.

The application of eq 16 to our quenching data resulted in plots which displayed a distinctly upward curvature. This implies that Stern–Volmer kinetics do not describe

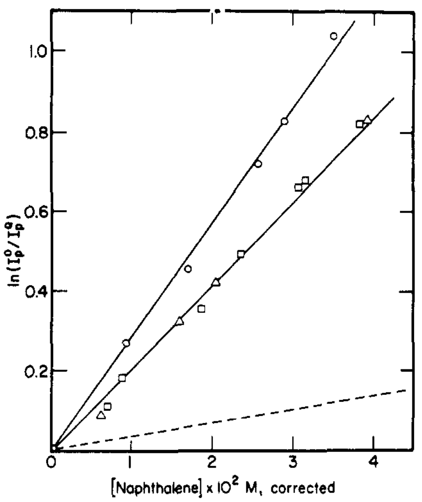

Figure 7. Perrin plots of phosphorescence quenching in solid solutions of PAP homopolymers: (○) i-PAP-2; (□) a-PAP-2; (△) a-PAP-1. (– – –) Theoretical line based on R_A = 11 Å.

the quenching behavior of our systems. Equation 16 is valid only in the case where energy migration is sufficiently rapid or occurs to such an extent that a statistical mixing of donor and acceptor groups is achieved during the excited-state lifetime of the former. This is clearly not the case here.

If energy migration in solid solutions of PAP is less efficient than that in the systems mentioned above, then the active-sphere model of Perrin[52] may better describe the observed behavior. The results of this are shown in Figure 7 and it can be seen that excellent straight lines are obtained. The naphthalene concentrations have been corrected for volume contraction encountered upon cooling the solutions to 77 K.

A Förster mechanism of energy transfer is highly unlikely as it involves a forbidden transition in both donor and acceptor. Furthermore, the overlap between donor emission and acceptor absorption spectra is negligible. Energy transfer in the poly(acrylophenone)–naphthalene system should therefore occur by an exchange mechanism. In this case the radius of the active sphere, R_A, for the quencher is about 11 Å and our data points should lie on the dashed line drawn in Figure 7.

The much higher slopes that are obtained correspond to active spheres of quenching having radii of 22.5 and 20.3 Å for isotactic and atactic poly(acrylophenones), respectively. Failure to correct for volume contraction gives R_A values of 24.3 and 21.9 Å for each.

In the absence of material diffusion, the increased magnitude of the active sphere of quenching of naphthalene can only be explained by the occurrence of intramolecular energy migration in the polymers.[43] Excitation energy initially located on chromophores not within an active sphere of the quencher defined by a radius of 11 Å is able to migrate down the polymer chain and thereby enter this volume. Upon doing so it is quenched. This process would result in an "effective" active sphere of quenching which is much larger than the theoretical one.

The lack of a molecular weight effect as evidenced by the identical values of R_A for a-PAP-1 and a-PAP-2 can be taken to imply that the exciton migration length is shorter than the contour length of the polymer.[53] The invariance of the $k_q\tau_3$ values for a-PAP-1 and a-PAP-2 shown in Table II suggests that this is true in fluid solutions as well.

The higher value of R_A in the isotactic polymer in comparison to the atactic polymers indicates a greater extent of intramolecular energy migration in the former. This may be due to the greater number of intramolecular contacts in the more compact i-PAP coil. It also corroborates our earlier hypothesis that the increased curvature of the chain scission plots (Figure 2) for i-PAP as compared to a-PAP might arise as a result of increased intramolecular energy migration in the former. Such a process would clearly raise the efficiency of a chain-end quenching photoproduct.

Guillet et al.[54] have reported similar behavior for the phosphorescence quenching of a-PAP in solid 77 K solutions using *cis,cis*-1,3-cyclooctadiene as the acceptor. These authors obtained a value of 19 Å for R_A, uncorrected for volume contraction effects. In comparison, our value of 21.9 Å probably reflects an increased efficiency of quenching when naphthalene is the acceptor. David et al.[43,55] have reported values of 26 and 36 Å for phosphorescence quenching by naphthalene in films of atactic poly(acrylophenone) and poly(vinylbenzophenone), respectively.

The direct comparison to Perrin quenching radii reported by other workers should be done with care. For example, the consideration of our uncorrected R_A value of 21.9 Å for a-PAP in terms of the higher values quoted by Geuskens might be taken as being indicative of an increased efficiency of energy migration due to the possibility of an inter- as well as an intramolecular process in the films. While this conclusion may well be true, other factors may also be involved.

For example, in the derivation of the Perrin equation, the calculation of the probability that an excited donor lies within the active sphere of a quencher involves the assumption of an isotropic mixture of the two. This condition is not met in solid solutions of polymers where the chromophores are found in concentrated regions. Preferential solvation of the quencher, inside or outside of the polymer coil prior to freezing, may also be a factor. Both effects make direct comparisons of film and solid solution results a difficult task.

However, we can say that from comparison of our R_A values, intramolecular energy migration certainly occurs to a greater extent in the isotactic than in the atactic polymer. That this result is also applicable to the macromolecules in fluid solution is supported by the results of Ishii et al.,[4] who have reported energy migration coefficients Λ of 6.0×10^{-5} and 14.4×10^{-5} cm^2 s^{-1} for atactic and isotactic polystyrene in such media.

Conclusions

While the quantum yield of chain scission in poly(acrylophenone) is independent of tacticity, its inhibition by naphthalene is not. This can be attributed to a more facile γ-hydrogen abstraction process in the isotactic polymer, resulting in a shorter triplet lifetime.

Intramolecular energy transfer occurs to a greater extent in isotactic poly(acrylophenone) than in its atactic analogue, both in room-temperature fluid solutions and 77 K solid matrices. An increased number of interchromophore contacts in the isotactic polymer may well be responsible for this effect. Evidence for this arises from the solution properties of the polymers, these being strongly suggestive of a more orderly packing arrangement for the isotactic chain.

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References and Notes

(1) Longworth, J. W. *Biopolymers* **1966**, *4*, 1131.
(2) Ishii, T.; Matsushita, H.; Handa, T. *Kobunshi Ronbunshu* **1975**, *32*, 211.
(3) Ishii, T.; Matsunaga, S.; Handa, T. *Makromol. Chem.* **1976**, *177*, 283.
(4) Ishii, T.; Handa, T.; Matsunaga, S. *Makromol. Chem.* **1977**, *178*, 2351.
(5) David, C.; Putman-DeLavareille, N.; Geuskens, G. *Eur. Polym. J.* **1974**, *10*, 617.
(6) Tanaka, H.; Otsu, T. *J. Polym. Sci.* **1977**, *15*, 2613.
(7) Kilp, T.; Guillet, J. E.; Merle-Aubry, L.; Merle, Y., submitted to *Macromolecules*.
(8) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146.
(9) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1972**, *5*, 410.
(10) Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.
(11) Kilp, T.; Houvenaghel-Defoort, B.; Panning, W.; Guillet, J. E. *Rev. Sci. Instrum.* **1976**, *47*, 1496.
(12) Jellinek, H. H. G. "Stereochemistry of Macromolecules"; Ketley, A. D., Ed.; Marcel Dekker: New York, 1968; Vol. 3.
(13) Saito, O. "The Radiation Chemistry of Macromolecules"; Dole, M., Ed.; Academic Press: New York, 1972; Vol. 1.
(14) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
(15) Lukac, I.; Hrdlovic, P.; Manasek, Z.; Bellus, D. *J. Polym. Sci., Part A-1* **1971**, *9*, 69.
(16) George, G. A. *J. Polym. Sci., Part A-2* **1972**, *10*, 1361.
(17) D'Alagni, M.; DeSantis, P.; Liquori, A. M.; Savino, M. *J. Polym. Sci., Part B* **1964**, *2*, 925.
(18) Pino, P.; Ciardelli, F.; Lorenzi, G. P.; Montagnoli, G. *Makromol. Chem.* **1963**, *61*, 207.
(19) Natta, G. *Makromol. Chem.* **1960**, *35*, 94.
(20) Danusso, F.; Moraglio, G. *J. Polym. Sci.* **1957**, *24*, 161.
(21) Faure, J.; Fouassier, J.-P.; Lougnot, D.-L.; Salvin, R. *Eur. Polym. J.* **1977**, *13*, 891.
(22) Oster, A.; Nishijima, Y. *Adv. Polym. Sci.* **1964**, *3*, 313.
(23) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815.
(24) Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1975**, *97*, 4817.
(25) Parker, C. A.; Joyce, T. A. *Trans. Faraday Soc.* **1968**, *65*, 2823.
(26) Schuster, D. I.; Weil, T. M. *J. Am. Chem. Soc.* **1973**, *95*, 4091.
(27) Singer, L. A.; Brown, R. E.; Davis, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 8638.
(28) Lewis, F. D. *Tetrahedron Lett.* **1970**, 1373.
(29) Lewis, F. D. *J. Phys. Chem.* **1970**, *74*, 3332.
(30) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212.
(31) Shimanouchi, T.; Tasumi, M.; Abe, Y. *Makromol. Chem.* **1965**, *86*, 43.
(32) Bovey, F. A.; Hood, F. P., III; Anderson, E. W.; Snyder, L. C. *J. Chem. Phys.* **1965**, *42*, 3900.
(33) Merle-Aubry, L. Ph.D. Thesis, University of Rouen, France, 1975.
(34) Ware, W. R.; Novros, J. S. *J. Phys. Chem.* **1966**, *70*, 3247.
(35) Yguerabide, J.; Dillon, M. A.; Burton, M. *J. Am. Chem. Soc.* **1964**, *40*, 3040.
(36) Heskins, M.; Guillet, J. E. *Macromolecules* **1970**, *3*, 231.
(37) Gorrel, J. H.; Dubois, J. T. *Trans. Faraday Soc.* **1967**, *63*, 347.
(38) Weyl, D. A. *Spectrochim. Acta, Part A* **1962**, *24*, 1017.
(39) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(40) Takemura, T.; Baba, H.; Fujita, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2625.
(41) Voltz, R.; Laustriat, G.; Coche, A. *J. Chim. Phys.* **1963**, *63*, 1253.
(42) Faure, J.; Fouassier, J.-P. Lougnot, D.-J.; Salvin, R. *Nouv. J. Chim.* **1977**, *1*, 15.
(43) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 537.
(44) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 417.
(45) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(46) David, C.; Putman, N.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 409.
(47) Powell, R. C. *J. Chem. Phys.* **1971**, *55*, 1871.
(48) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953; p 313.
(49) Birks, J. B.; Leite, M. S. C. P. *Proc. Phys. Soc. (Adv. Mol. Phys.)* **1970**, *3*, 513.
(50) David, C.; Naegelen, V.; Piret, W.; Geuskens, G. *Eur. Polym. J.* **1975**, *11*, 569.
(51) David, C.; Baeyens-Volant, D.; Macedo de Abreu, P.; Geuskens, G. *Eur. Polym. J.* **1977**, *13*, 841.
(52) Perrin, F. *C. R. Hebd. Seances Acad. Sci.* **1924**, *178*, 1978.
(53) Pasch, N. F.; Webber, S. E. *Macromolecules* **1978**, *11*, 727.
(54) Dan, E.; Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 228.
(55) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 1405.

Quantitative Analysis of the Strain Energy Density Function for *cis*-1,4-Polyisoprene Rubber Vulcanizate

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ABSTRACT: A quantitative analysis of the strain energy density function for an isoprene rubber vulcanizate is carried out based on the experimental biaxial stress–strain data presented in a previous paper. The form of the strain energy density function is $W = CT(I_1 - 3) + \beta(I_1,I_2)$, which was derived in the previous paper by measuring its derivative forms with respect to I_1 and I_2, the first and second invariants of the deformation tensor. First, the stresses along the two principal directions are integrated to evaluate the strain energy density as a function of I_1 and I_2; then the function $\beta(I_1,I_2)$ is determined based on the functional form of W given above. It is observed that the function $\beta(I_1,I_2)$ represents between 0.32 and 0.46 of the total energy W for all deformations examined in this experiment and that it decreases with increasing deformation such that, for example, the amount is 0.41 at $I_1 = I_2 = 5$ and 0.36 at $I_1 = I_2 = 10$ in the case of pure shear deformation. In order that this result can be compared with those of other researchers, the ratio f_e/f (where f is the uniaxial tensile stress and f_e is the energetic component which is considered to be caused by the internal energy change accompanying the deformation) is derived from the biaxial experiment and discussed.

Introduction

In an earlier paper,[1] an expression for the strain energy density function, W, for a vulcanized *cis*-1,4-polyisoprene rubber was developed from an experimental survey in which a biaxial extension technique was used. The function W presented has a simple form comprising two separate terms, one term directly proportional to absolute temperature, the other, independent of temperature; the latter is a complicated function of the deformation as shown in eq 1:

$$W = CT(I_1 - 3) + \beta(I_1,I_2) \tag{1}$$

Here C is a constant, T is the absolute temperature, and $\beta(I_1,I_2)$ is a function only of deformation expressed by I_1