Photochemistry of Ketone Polymers. 15. Studies of the Photochemistry of Isotactic and Atactic Poly(acrylophenones)

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ABSTRACT: The effect of tacticity upon the photodegradation of poly(acrylophenone) in fluid solution has been investigated. The quantum yield of main-chain scission via the Norrish type II reaction was found to be approximately 0.40 for both isotactic and atactic homopolymers in toluene solution. The behavior is rationalized on the basis of identical local conformations for the biradical intermediates. The ineffectiveness of low levels of an added Lewis base in enhancing the quantum yield may be attributable to an intramolecular biradical stabilization mechanism.

Introduction

The effect of tacticity on polymeric photoprocesses has only recently come under intensive investigation. Most studies in this regard have dealt with excimer formation in polystyrene. Vala et al.[1] have reported that the solution fluorescence spectra of polystyrene is independent of tacticity. However, subsequent results published by Longworth[2] and Ishii et al.[3-5] indicate that the ratio of excimer and monomer emission intensities, I_e/I_m, is considerably higher in the isotactic polymer. Ishii has found that the rate constants are higher and activation energies lower for excimer formation in isotactic polystyrene as compared to the atactic polymer. David et al.[6] have studied the effects of orientation, tacticity, and crystallinity in polystyrene films. Their results show that the ratio I_e/I_m at 77 K increases according to the sequence atactic < atactic oriented < isotactic amorphous < isotactic crystallized, again demonstrating the importance of increasing polymeric stereoregularity.

The effects of tacticity in polymer photodegradation have not received the same attention, and it appears that only one paper dealing with this subject as it relates to the photochemistry of ketone-containing polymers has been published.[7]

Recently, the synthesis of poly(acrylophenone) (PAP) of a very high degree of isotacticity (>92%) has been reported by Merle-Aubry et al.[8] The high tacticity was confirmed by ^{1}H and ^{13}C NMR studies. These authors also demonstrated that poly(acrylophenone) synthesized by free radical catalysts was primarily atactic. In view of the above-mentioned differences in the photophysical processes observed in polystyrene, it was thought that an investigation of some aspects of its photochemistry would prove to be of interest.

Previous studies on PAP have been reported by David et al.[9] and by Lukac et al.[10] Further work was published by Golemba and Guillet.[11] More recent results have been reported by Beck et al.[12] and by Faure et al.[13]

Experimental Section

The quantum yields for main-chain scission were determined for the polymers in solution at 30 °C.

Fisher ACS reagent grade benzene and toluene were used as solvents. They were dried overnight on $CaCl_2$ or $MgSO_4$ and freshly distilled prior to use. Purity checks were made by UV absorption spectra.

Irradiations were done with light of either 313- or 364-nm wavelength, isolated from a 250-W medium-pressure mercury arc lamp (Associated Electrical Industries, ME/D, box type) by the use of Schott narrow-band (Jena UV-PIL) interference filters. All solutions were thoroughly purged by dry nitrogen prior to the start of irradiation. The relative intensities of the light incident upon and transmitted by the quartz irradiation cell when filled with polymer solution were measured by a pyroelectric radiometer (Molectron Corp., Model PR200) placed immediately behind the cell. Potassium ferrioxalate actinometry was used to relate the digital display of the radiometer to an absolute value for the number of quanta incident per unit time.

The extent of degradation of the polymers was measured after set intervals of irradiation, using the technique of automatic viscometry, previously described by Kilp et al.[14] The total number of moles of chain breaks, S, can be calculated from

$$S = [(\bar{M}_n{}^0/\bar{M}_n) - 1]g/\bar{M}_n{}^0 \qquad (1)$$

where g is the weight in grams of the irradiated polymer and $\bar{M}_n{}^0$ and $\bar{M}_n$ are the initial and final number-average molecular weights, respectively. As shown by Amerik and Guillet,[15] however, this can be very well approximated with a minimum of error by

$$S = 2[(\bar{M}_v{}^0/\bar{M}_v) - 1]g/\bar{M}_v{}^0 \qquad (2)$$

where $\bar{M}_v{}^0$ and $\bar{M}_v$, viscosity-average molecular weights, are determined by a measurement of the intrinsic viscosity of the solution and application of the Mark–Houwink equation. The validity of this assumption has subsequently been verified by Nemzek and Guillet[16] for polymers whose initial polydispersity, $\bar{M}_w/\bar{M}_n$, lies between the values of 1.5 and 2.5.

The quantum yield of chain scission is then given by

$$\phi_{cs} = S/It \qquad (3)$$

where I is the number of photons (in einsteins) absorbed by the polymer per unit time and t is the period of irradiation.

Isotactic PAP was prepared[8] by using diethylzinc as the initiator in a dry, oxygen-free nitrogen atmosphere. (Conditions: 0.5 mol % at 0 °C during 1 month; the isotactic fraction (30%, mp 240 °C) was extracted with cold acetone 4 times.) The technique was that originally reported by Tsuruta et al.[17] The PAP thus prepared contained a degree of isotacticity of greater than 92% as determined by ^{1}H and ^{13}C NMR spectra. Two samples were used in these studies, i-PAP-1 and i-PAP-2, differing in their number-average molecular weights. These were 274 000 and 470 000, respectively.

Two samples of atactic PAP were prepared. A low molecular weight polymer, a-PAP-1, was prepared by bulk polymerization. Acrylophenone monomer (20 g) was placed in a Pyrex tube along with 0.01 g (0.05 wt %) of azobis(isobutyronitrile) (AIBN) initiator. Following degassing by five freeze–thaw cycles on a high-vacuum line (10^{-4} torr) the tube was sealed off under vacuum. It was then placed into an oil bath at 65 °C for 36 h. Following this time, the tube was opened and the polymer was precipitated into methanol. Purification was accomplished by five cloud point reprecipitations of the polymer in a 2% toluene solution into an excess of methanol, a nonsolvent. The polymer was dried for 48 h at 1 torr by placing it into a vacuum desiccator connected to a rotary pump. The recovered polymer weighed 1.8 g, corre-

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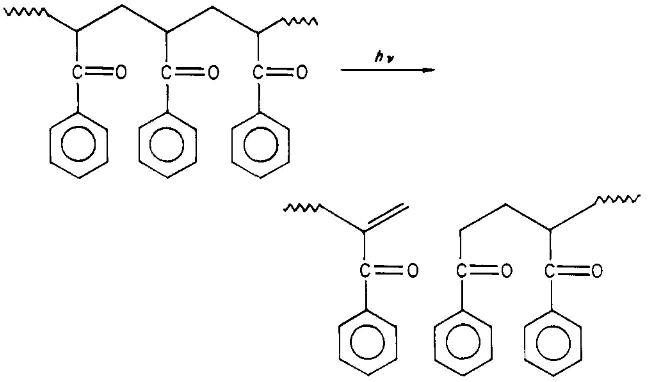
sponding to a conversion of 10%. $\bar{M}_n$ via osmometry was found to be 70 000.

Thermally initiated free radical polymerization to form high molecular weight PAP, a-PAP-2, was attempted unsuccessfully using a wide variety of reaction conditions and initiators. Only polymers with $\bar{M}_n$ between 50 000 and 70 000 were obtained. As a result, this polymer was prepared by a low-temperature free radical bulk polymerization process using bis(4-*tert*-butylcyclohexyl)peroxy dicarbonate as the initiator. A mixture of 5.2 g of monomer and 0.01 g of initiator was degassed and sealed off as above. Polymerization was carried out for 63 h at 32 °C. Since the half-life of the initiator is 55 h at this temperature, roughly 0.1 wt % of the initiator should have decomposed during this time. Recovery, purification, and drying were as outlined above. The yield was 2.6 g, corresponding to a conversion of 50%. A number-average molecular weight of 360 000 was obtained.

As aromatic ketones absorb light of wavelength greater than 300 nm quite efficiently, all polymer syntheses, solution preparations, and subsequent photolyses were carried out in a dark room. A red safety lamp was used for illumination. This eliminated effects due to exposure to the output of the fluorescent room light.

Results and Discussion

Irradiation of 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 Norrish type II photochemical reaction, resulting in a polymer main-chain scission, hence reducing its molecular weight.



Although the Norrish type I cleavage would also result in a slight decrease in molecular weight due to the loss of a benzoyl group, the viscosity of the solution would not be significantly affected since the decrease in polymer hydrodynamic volume would be negligible. In any event, the extent of type I scission is likely very small as the sum of all quantum yields other than type II is less than 0.01 in the model compound isobutyrophenone.[18] Further support for the lack of the type I process arises from the results of David et al.,[9] who report that no benzaldehyde or gel formation occurs when even very concentrated solutions of a-PAP are irradiated.

Initial studies were carried out on the polymers a-PAP-1 and i-PAP-1. In preliminary studies in benzene solution molecular weights were calculated by using the viscosity relationship

$$[\eta] = (2.82 \times 10^{-5})M^{0.84} \qquad (4)$$

the constants being those determined by Lukac et al.[10] for PAP in benzene. Although these parameters were determined for an atactic sample, it was assumed that the values for the isotactic sample will not be greatly different. This procedure may be justified by results of other studies. Danusso and Moraglio,[19] for example, have reported that no difference exists in the viscosity–molecular weight relationship for fractionated samples of atactic and isotactic polystyrene in toluene solution.

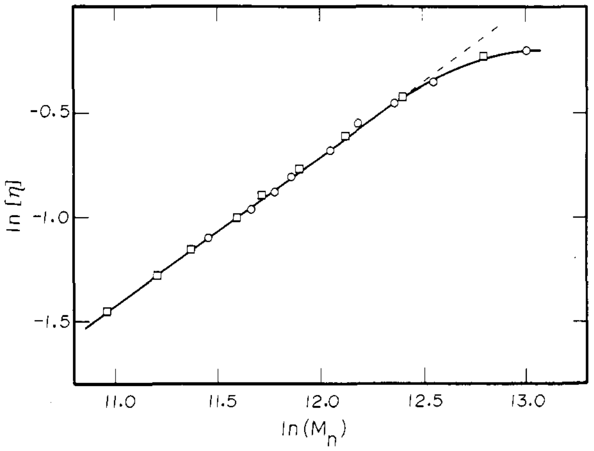


Figure 1. Viscosity–molecular weight relationship for PAP homopolymers: (○) i-PAP-2; (□) a-PAP-2; (——) curve-fit result. Toluene solutions at 30 °C.

Quantum yields for main-chain scission in benzene solution were 0.34 ± 0.02 and 0.37 ± 0.02 for the isotactic and atactic polymers, respectively.

The procedure outlined by Kilp and Guillet[20] was used to determine the viscosity–molecular weight relationship for i-PAP-2 and a-PAP-2 in toluene. In this procedure samples of known distribution are obtained by photolysis of the original polymer in solution. Aliquots are removed for viscosity and molecular weight determination by osmometry.

The double-logarithmic plot for intrinsic viscosity vs. molecular weight for a-PAP-2 and i-PAP-2 is shown in Figure 1. It can be seen that both polymers lie on a common curve. This independence of tacticity is identical with the behavior of polystyrene in toluene, as reported by Danusso and Moraglio[19] and provides further support for the previous assumption of identical K and a values for the polymers in benzene solutions.

The direction of departure from linearity in Figure 1 would indicate that both polymers possess an original polydispersity of less than 2.[20] Since initially a-PAP-2 lies closer to the straight line corresponding to samples possessing the most probable distribution, characterized by $\bar{M}_w/\bar{M}_n = 2.0$, it has a higher polydispersity than does i-PAP-2.

A linear regression analysis of the collinear points in Figure 1 results in the following relationship:

$$[\eta] = (2.82 \times 10^{-5})\bar{M}_n^{\,0.72} \qquad (5)$$

or, alternatively

$$[\eta] = (1.71 \times 10^{-5})\bar{M}_w^{\,0.72} \qquad (6)$$

However, this result was not used in the subsequent studies of the photodegradation of i-PAP-2 and a-PAP-2. As seen from Figure 1, use of this relationship in the early stages of degradation would give molecular weights lying on the dashed line and would therefore be erroneous. While the magnitude of the resultant error in the calculation of chain scissions is reduced by virtue of the use of the ratio $\bar{M}_v^{\,0}/\bar{M}_v^{\,t}$ in eq 2, it remains in the factor $2/M_v^{\,0}$. Therefore, this relationship is presented for use only in the case where the entire viscosity–molecular weight plot is not available.

The derivation of molecular weights from measurements of solution viscosities was therefore accomplished by the application of a curve-fit computer routine to the data in Figure 1. For the best results, the experimental points were fit to a seven-term polynomial

$$\ln (\bar{M}_n) = B_1 + B_2(\ln [\eta]) + \ldots + B_7(\ln [\eta])^6 \qquad (7)$$

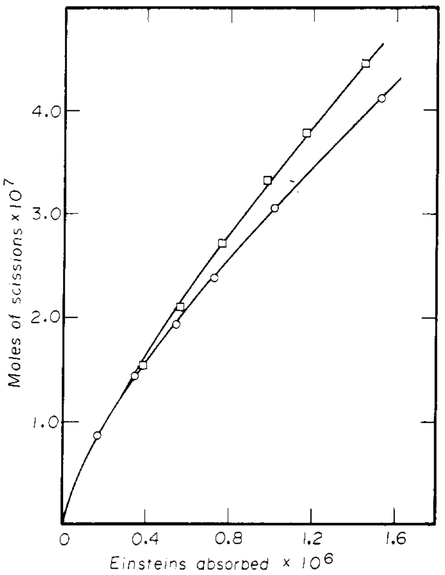


Figure 2. Photolysis of PAP homopolymers in toluene solutions, 364 nm, 30 °C: (○) i-PAP-2; (□) a-PAP-2. Solutions were 1.9 × 10^{-2} M in carbonyl units. Absorbed dose rate was 4.8 × 10^{-7} einstein L^{-1} s^{-1}.

with the values of the coefficients B_1 to B_7 being 14.43, 10.44, 19.83, 14.00, −8.75, −16.74, and −6.22, respectively. This gave an excellent fit, as evidenced by the solid line in Figure 1, with the sum of the squares of deviations of the fitted values from the input values of ln ($\bar{M}_n$) being only 1.64 × 10^{-3}. Molecular weights as a function of irradiation time were then calculated by inserting the measured value of ln [η] into eq 7.

This procedure has the additional advantage of yielding number-average molecular weights, hence allowing the use of eq 1 for the determination of the number of main-chain scissions. Therefore no corrections for initial polydispersities, as outlined by Nemzek and Guillet,[16] are required.

The results of the irradiation of i-PAP-2 and a-PAP-2 at 364 nm in toluene solutions at 30 °C are shown in Figure 2. It can be seen that the initial slopes for each are virtually identical, divergence only occurring at values corresponding to one chain break or more per original polymer molecule. The quantum yields of main-chain scission as calculated from the initial slopes are 0.41 ± 0.01 and 0.40 ± 0.01 for i-PAP-2 and a-PAP-2, respectively.

Table I lists the results of the quantum yields determined in a variety of solvents at 313 and 364 nm. Two further experiments were conducted in toluene–5% methanol solution. Results for these were calculated by using the same [η]–$\bar{M}_n$ relationship as derived for a-PAP-2 and i-PAP-2 in neat toluene. Higher concentrations of methanol were not used as these resulted in the formation of distinctly hazy polymer solutions.

The quantum yield of main-chain scission in PAP would seem to be independent of irradiation wavelength as well as the tacticity of the polymer degraded. The lower value of 0.34 for i-PAP-1 in benzene is in all probability due to the larger inherent error in calculating quantum yields from the initial slopes of chain scission plots when these correspond to extensive degradation (vide infra).

The independence of chain scission quantum yields with respect to polymeric stereoregularity is in contrast to results reported by Tanaka and Otsu.[7] These authors have found that atactic poly(*tert*-butyl vinyl ketone) is degraded more efficiently than its isotactic analogue. They attributed their observed results to variations in steric interactions due to differences in polymer conformation with tacticity. The exact nature of these effects was not elaborated.

Table I
Quantum Yields of Main-Chain Scission in PAP Homopolymers

polymer	irradiation conditions	ϕ_{II}[a]
i-PAP-1	313 nm, benzene,[b] 30 °C	0.34 ± 0.02
a-PAP-1	313 nm, benzene,[b] 30 °C	0.37 ± 0.02
i-PAP-2	364 nm, toluene,[c] 30 °C	0.41 ± 0.01
a-PAP-2	364 nm, toluene,[c] 30 °C	0.40 ± 0.01
i-PAP-2	364 nm, toluene[c] + 5% MeOH, 30 °C	0.39 ± 0.01
a-PAP-2	364 nm, toluene[c] + 5% MeOH, 30 °C	0.41 ± 0.01

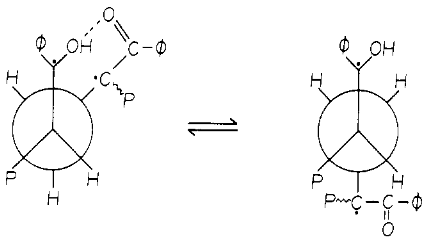
[a] Quantum yield of main-chain scission for solutions 1.9 × 10^{-2} M in carbonyl units and an absorbed dose rate of 4.8 × 10^{-7} einstein L^{-1} s^{-1}. [b] Using values of K and a from Lukac et al.[10] [c] Using curve-fitting procedure.

The quantum yield values listed in Table I are somewhat higher than the values of 0.22 and 0.25 previously reported by Lukac et al.[10] and by Golemba and Guillet.[11] They are, however, in better agreement with values reported for the small-molecule model compound butyrophenone,[18] which has been reported as 0.43.

It should be noted that plots of chain scission vs. irradiation time, as shown in Figure 2, are not linear but exhibit a slight curvature, even very early in the irradiation. This behavior is quite likely attributable[23] to quenching of the triplet carbonyls by the vinyl ketone photoproducts of chain scission. Thus quantum yields determined from initial slopes are very dependent upon the initial data points. With the increased accuracy obtained from automatic viscometry one is able to obtain more reliable results in this region. Since the slopes of these plots are directly proportional to the quantum yield of chain scission, these values will be higher than those obtained by sampling later on. Estimates of 0.4–0.6 for the quantum yield of chain scission in a-PAP as determined by laser flash photolysis have been reported by Beck et al.[12] It can be seen that our values in the range 0.37–0.41 are in better agreement with this recent work. However, it should be noted that Faure et al.[13] have also reported a value of 0.24 for ϕ_{II} in a-PAP as determined by a viscometric technique.

The invariance of quantum yields for main-chain scission upon the addition of 5% methanol is similar to behavior previously reported by David et al.[9] It is interesting in view of the solvation effects of Lewis bases on the efficiency of β cleavage in small-molecule alkyl aryl ketones as reported by Wagner.[21] In these cases, large increases in type II quantum yields are obtained due to stabilization of the 1,4-biradical via hydrogen bonding to the Lewis base, thereby reducing the extent of hydrogen back-transfer to form ground-state reactant. Recently, however, Salvin et al.[22] reported that the quantum yield of photoproduct formation in 1,3-dibenzoylpropane is independent of solvent polarity, implying that in this case intramolecular stabilization of the 1,4-biradical is the major factor. Their model is based on mechanisms, originally proposed by Wagner,[23,25] to account for increased ϕ_{II} values in δ-methoxyvalerophenone as well as in highly concentrated solutions of valerophenone. A similar mechanism may be operative in the polymeric case.

Golemba and Guillet[11] have shown that the short excited-state lifetime (~10^{-9} s) of a-PAP in solution is due to the very efficient abstraction of γ hydrogens (k_H ~10^7 s^{-1}). This has subsequently been verified by Faure et al.[24] In this case, it is important to realize[26] that the quantum yield of type II scission reflects the behavior of the 1,4-



(a) (b)

Figure 3. Intramolecular stabilization of biradical intermediate in PAP.

biradical intermediate and not the excited-state precursor. Experimental ϕ_{II} values then are a function of the partitioning of the 1,4-biradical between the pathways leading to bond scission and reversion to ground-state reactant via back-transfer of the abstracted hydrogen. If γ-hydrogen abstraction is not the rate-controlling step, then the subsequent quantum yields of chain scission will reflect the behavior of the biradical intermediates.

Recently, Merle-Aubry and Merle[27] have made ^{1}H NMR studies of the conformation of the isomeric[2,4] dibenzoylpentanes, which are possible model compounds for poly(acrylophenone). They found that the most probable conformations for the syndio dyads were tt and g^+g^+, whereas g^-t and tg^+ were favored in the isotactic dyads. Since the g^+g^+ conformation does not give a close approach of the carbonyl to the γ hydrogen, the independence of the scission quantum yields on tacticity is further evidence that the rate-limiting step is not γ-hydrogen abstraction but the reversion of the biradical intermediate to the observed products.

Upon abstration of a γ hydrogen, the γ carbon becomes sp^2 hybridized and loses all sense of chirality. Therefore, from simple molecular models it can be seen that both a-PAP and i-PAP are able to form identical conformers, as shown in Figure 3a, where P denotes the polymer chain.

The dashed line in Figure 3a indicates the stabilization of the biradical by hydrogen bonding. It can also be seen that equal energy barriers in both polymers must be overcome to allow rotation to the conformation most propitious for β cleavage, as shown in Figure 3b.

The noneffectiveness of Lewis bases in raising type II quantum yields is then seen to be a consequence of the intramolecular stabilization of the polymeric 1,4-biradical. This is not possible for molecules such as butyrophenone and valerophenone in dilute solutions. Hence, these compounds do show an increase in ϕ_{II} with increasingly larger amounts of added Lewis bases.

Since equal stabilization of the biradical occurs for both a-PAP and i-PAP via this mechanism and identical rotational energy barriers must be overcome to achieve a conformation most amenable to β cleavage, it is not surprising that both polymers have identical ϕ_{II} values. Tacticity therefore probably only affects the fate of γ-hydrogen abstraction. If the latter is sufficiently high in comparison to the subsequent cleavage of the 1,4-biradical, no dependence on polymeric stereoregularity should be observed. The differences reported by Tanaka and Otsu[7] for atactic and isotactic poly(*tert*-butyl vinyl ketone) probably reflect the inherently lower rate of hydrogen abstraction by aliphatic ketones. Quantum yields in this case will be determined not only by the behavior of the 1,4-biradical but also by the ease with which it is formed. Thus, initial polymeric conformation will play a significant role.

Conclusions

The quantum yield of main-chain scission via the Norrish type II photoreaction is independent of the tacticity of the PAP homopolymers. This behavior can be attributed to a very fast γ-hydrogen abstraction process coupled with the availability of identical local conformations for the biradical intermediates. The addition of low levels of the Lewis base methanol fails to enhance the quantum yields of degradation. An intramolecular stabilization mechanism for the biradical intermediates may well be responsible for this.

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