Abstract

Laser flash photolysis of an alternating copolymer of phenyl isopropenyl ketone with styrene was studied (25 ns laser flash of 347 nm light). Transient absorption spectrum obtained immediately after the end of the flash was due to a triplet-triplet absorption of benzoyl chromophore. Since a fraction of the triplet state was decayed by the triplet-triplet annihilation, a triplet decay rate constant was determined to be $8.7 \times 10^6 \text{s}^{-1}$ from the extrapolation of the absorbed photons at zero. Quantum yields of the triplet formation and the $\alpha$-cleavage reaction are estimated to be 0.6 and 0.3, respectively. Quenching rate constants by naphthalene and oxygen are $(9 \pm 1) \times 10^9 \text{l/mol.s}$. These bimolecular rate constants with the T-T annihilation are larger (1.5 to 3 times) than those of homopolymer and random copolymers.

1. Introduction

It is well known that a bond between a tertiary and a carbonyl carbon is easily cleaved from a n-$\pi^*$ excited state of the carbonyl group. In polymer samples, the Norrish Type I reaction for the resulting uneffective main chain degradation are reported by a few papers. Since this process forms radicals at high quantum yield, it seems easy to design UV curing resin and electron beam lithography by applying the reaction. Sensitization as the radical chain reaction is possible.

The photolysis of poly methyl isopropenyl ketone (PMIK) which shows a radical process is a typical example by means of the basis of linear photocatalysis on the image formation. The system is based on acid catalysis of the aldol condensation of PMIK. PMIK resist for electron beam lithography was reported by Levine et al. Tsuda et al. investigated highly sensitized PMIK resists having practical sensitivities for specified light sources. The Problem of practical use on vinyl ketone polymers has been studied by many researchers.

* Received August 7, 1981
The authors have studied the photolysis of the polymer samples such as PMIK\(^2\), poly tert-butyl vinyl ketone (PBVK)\(^3\), and poly phenyl isopropenyl ketone (PPIK)\(^4\) for the application of the image formation.

The chemical reactions may be occurred at some special configurations for the reaction after the energy migration from the chromophore by absorbing light\(^10\). Recently, Scaiano et al.\(^11\) estimated the rate of the energy migration along the polymer chain was about 30 ps on the degradation of copolymer of phenyl vinyl ketone with o-tolyl vinyl ketone.

This paper reports results of a laser flash photolysis of an alternating copolymer phenyl isopropenyl ketone (PIK) with styrene (St) for an aid of the fundamental study of image formation (not only the photodegradation but also the photocycloaddition). The results obtained are compared with them of homo-(PPIK) and random copolymers with St.

2. Experimental

Poly isopropenyl ketone (PIK) was synthesized by a Mannich type reaction from propiophenone and paraformaldehyde\(^12\). PIK coordinated with stannic chloride ([SnCl\(_4\)])/[PIK]=1/4) was copolymerized with St in toluene at -20°C ([PIK]=[St]=2.0 mol/l). A polymerization was initiated by a precipitation in methanol. After four hours, the polymerization was stopped by a precipitation in methanol. Polymer obtained was purified by the reprecipitations, three times by hydrochloric acid-methanol solution (10 v/v % of HCl acid) and twice with cyclohexane. Polymer yield was about 5%. An alternating tendency was checked by an elementary analysis and spectroscopies\(^13\). Molecular weight of the polymer was measured by vapour pressure measurement with aid of a Hitachi-Perkin-Elmer apparatus (model 115) and GPC with aid of a Toyosoda apparatus (model 802) (Mn=2.4×10\(^5\)).

Benzene was purified by washing five times with sulfuric acid and five times with distilled water. After drying on calcium chloride and calcium hydride, benzene was distilled twice using a splitting-tube column.

A ruby laser apparatus was described before\(^14\). By choosing a polymer concentration (0.52 g/l), optical density at \(\lambda=347\) nm was kept as 0.1. Normally 8.9×10\(^{-8}\) Einstein of photons were flashed.

3. Results

Figure 1 illustrates transient absorption spectra obtained with benzene solution immediately at the end of the flash and at 0.7 \(\mu\)s after the flash. The spectrum immediately at the end of the flash exhibits absorption maxima below 300 nm and at 470 nm. At 0.7 \(\mu\)s, the spectrum hasn’t the absorption maximum at 470 nm, but has below 300 nm and at 380 nm. This spectrum strongly resembled to benzoyl radical reported previously by authors\(^9\) in a good agreement, and has similarity with triplet absorption spectra of poly phenyl vinyl ketone (PPVK)\(^14\) and PPIK\(^4\).

The decays of the transient absorption are demonstrated in Figure 2. Above \(\lambda=480\) nm, the absorption decreased to near zero by first-order kinetics so that only one species could
be attributed in the decay. If the absorption of a short-lived species monitored below 480 nm decayed by the same kinetics, a build-up of the absorption of a long-lived species can be detected after the subtraction of the absorption of the short-lived species from an oscilloscope trace. It seems that the absorption immediately after the end of the flash is shown only by the short-lived species and the long-lived species is formed from the short-lived species by first-order kinetics. The decay rate of the short-lived species and the formation rate of the long-lived species were constants respectively over all the wavelength monitored at same absorbed photons.

For analyzing the short-lived species, an effect of absorbed photons on the signal intensity and on the decay rate was studied.

![Fig. 1 Transient absorption spectra observed A (- - - -): immediately after the flash and B (---): 0.7 μs after the flash in benzene solution.](image1)

![Fig. 2 First-order plots demonstrating the decrease of the short-lived absorption and the increase of the long-lived absorption (dotted line) monitored at λ=320 nm (a), 300 nm (b), and 520 nm (c). Dotted lines demonstrate the plots of (d∞-d)/d∞ vs. time. Absorbed photon per flash: ca. 1.4×10⁻⁵ einstein/l.](image2)
Figure 3 shows the change of optical densities of transient absorptions and the rates monitored at \(\lambda=320\) nm in the absorbed photons. As the optical densities were increased with the absorbed photons, it showed that this photolysis was a single photon process.

The decay rate of the short-lived species was increased with the absorbed photons, though the formation rate of the long-lived species was constant \([k=(4\pm1)\times10^6\,\text{s}^{-1}]\). The decay rate constant of the short-lived species was obtained to be \(8.7\times10^6\,\text{s}^{-1}\) by an extrapolation of the absorbed photons at zero. On a quenching by naphtalene as a triplet quencher, the formation of naphtalene triplet was also detected in PPIK or pivalophenonenaphtalene system\(^6\). It was concluded from the above facts that the short-lived species was due to triplet state of benzoyl group and the increase of the decay rate with the absorbed photons was based on triplet-triplet annihilation, that is, one of typical triplet characters.

In order to determine the rate constant \(k_q\) of a reaction of the triplet ketone with singlet naphtalene (\(S_0\)) as a triplet quencher, the optical densities immediately after the flash and after 1 \(\mu\)s and 2 \(\mu\)s successive period from the end of the flash were monitored at \(\lambda=413\) nm by various quencher concentrations \((10^{-3}\sim3\times10^{-2}\,\text{mol/l})\). Figure 4 shows plots of the reciprocal optical density vs. the reciprocal quencher concentration. At 1 \(\mu\)s and 2 \(\mu\)s, straight lines were obtained. A linear relation was also obtained at the end of the flash and over
1.0 × 10⁻² mol/l of quencher concentration. In such case, it appears that the following relationship holds, where OD and OD₁ denote the optical density at several quencher concentration [Q] and the limiting optical density extrapolated to [Q]⁻¹=0.

\[ \text{OD}⁻¹ = \text{OD}₁⁻¹ + k_T \cdot \text{OD}₁⁻¹ \cdot k_q⁻¹ \cdot [Q]⁻¹ \]

From the straight lines at t=0 and 1 µs in Figure 4, the rate constant \( k_q \) was obtained to be 9 × 10⁸ l/mol.s. The quantum yield of the triplet state (\( \phi_T \)) was estimated to be 0.6 by means of the limiting optical density of the naphtalene triplet by the comparison with benzophenone-naphtalene system as \( \phi_T \) of benzophenone =1.00 (\( \phi_T \)=0.7 for PPIK, 0.5 for the random copolymer with St⁴). Absorbed photons were also determined to be 1.4×10⁻³ einstein/l by means of the quenching of benzophenone triplet by naphtalene [\( \varepsilon_3 = 413 \ \text{nm} = 2.8 \times 10^4 l/mol.cm (\text{Nap}*) \)].

Oxygen didn't affect the transient absorption spectrum but the decay rate of the transient species was accelated. A rate constant was estimated to be \( k_2 = (9 ± 1) \times 10^8 l/mol.s \).

**Figure 5** shows the transient absorption spectrum observed at 150 µs after the flash. The absorption maximum of benzyol radical at \( \lambda = 380 \ \text{nm} \) was deminished. It seemed that the spectrum at 150 µs was assinged as some polymer radicals which were decayed by second-order kinetics. Though an absorption coefficient was difficult to estimate, the optical density by a slope of the second-order plot was nearly constant at all the wavelength monitored. It seemed that only one transient species remained for several msec. order.

![Fig. 5 Transient absorption spectra monitored at 150µs after the flash. ---: Alternating copolymer of PIK with St, ---: PPIK, and ·······: Random copolymer of PIK with St containing 1 mol% of PIK unit.](image)
4. Discussion

Two important chemical processes on the triplet deactivation are possible in the photolysis of the alternating copolymer to induce Type I and II reactions by the following scheme.

\[ \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH} - \overset{\text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH} - + \text{Ph} - \text{CO} \cdot}{\text{hv}} \rightarrow \]

\[ (\text{Type I, } \alpha\text{-cleavage reaction}) \]

\[ \text{CH}_2 - \text{C} - \text{CH}_2 - \text{PH} \quad \rightarrow \text{Type II} \]

\[ (1, 4\text{-biradical}) \]

The results obtained show that the \( \alpha \)-cleavage reaction is the dominant chemical route. Ordinarily the life time of 1, 4-biradical intermediate on Type II reaction is too shorter than other radicals. It seemed that the signal of 1, 4-biradical couldn’t be detected for the overlap of the absorption signals of other radicals.

The quantum yield of \( \alpha \)-cleavage reaction \( (\phi_a) \) can be defined as the following equation,

\[ \phi_a = \phi_T \cdot \frac{k_a}{k_T} \]

where \( \phi_T \) is triplet quantum yield. The symbols of \( k_a \) and \( k_T \) are the rate constants of \( \alpha \)-cleavage reaction (the formation rate constant determined at \( \lambda = 320 \text{ nm} \)) and the triplet decay rate constant. \( \phi_a \) was determined to 0.3. And also, this quantum yield was estimated to be ca. 0.3 by comparing directly the signal intensity detected with them in PPIK and \( \alpha \)-hydroxyisobutylphenone\(^{16} \).

The rate constants of triplet-triplet annihilation (couldn’t be estimated exactly), \( k_{O_2} \) and \( k_q \) by naphtalene were larger than those of PPIK (1.5, 1.5, and 3 times larger respectively) and the random copolymer with St (1.5, 1.5, and 4 times larger). It suggests that the dependence of an energy migration in the polymer chain and the rate constants were closely related with a polymer configuration.

On the photolysis of an alternating copolymer of MIK with St, the quantum yield of main chain scission \( (\phi_{cs}) \) is about two times larger than a random copolymer of MIK with St (52 mol % of MIK unit in the copolymer). The stational irradiation of this copolymer wasn’t carried out but large \( \phi_{cs} \) would be expected.

It may be more effective to use the alternating copolymer of a photoreactive monomer with other monomers as photoresists than other random copolymers.

Reference

Studies of Image Formation by Vinyl Ketone Polymers

3) I. Naito, K. Imamura, H. Shintomi, and A. Kinoshita: will be published.