Acknowledgment. Research described here was supported by a grant from the National Science Foundation (DMR 86-10783). We are grateful to Prof. Paul Phillips for showing us preliminary data from his work on the polyethylene–acridine solids.

Registry No. Hexatriacontane, 630-06-8; naphthalene, 91-20-3; anthracene, 120-12-7; acridine, 260-94-6; benzoic acid, 65-85-0.

References and Notes

(1) Copley, G. N. *J. Chem. Educ.* **1959**, *36*, 596.
(2) Hsu, E. C.-H.; Johnson, J. F. *Mol. Cryst. Liq. Cryst.* **1974**, *27*, 95.
(3) Kerr, H. W.; Lewis, M. H. *Advances in Epitaxy and Endotaxy*; Schneider, H. G., Ruth, V., Eds.; Verlag: Leipzig, 1971; pp 147–164.
(4) Hunt, J. D.; Jackson, K. A. *Trans. Metall. Soc. AIME* **1966**, *236*, 843.
(5) Jackson, K. A.; Hunt, J. D. *Trans Metall. Soc. AIME* **1966**, *236*, 1129.
(6) Podolinskii, V. V. *Dokl. Akad. Nauk. SSSR* **1980**, *254*, 1168.
(7) Podolinskii, V. V.; Taran, Y. N.; Drykin, V. G. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1987**, *32*, 588.
(8) Smith, P.; Pennings, A. J. *Polymer* **1974**, *15*, 413.
(9) Pennings, A. J.; Smith, P. *Br. Polym. J.* **1975**, *7*, 460.
(10) Smith, P.; Pennings, A. J. *J. Mater. Sci.* **1976**, *11*, 1450.
(11) Smith, P.; van Ekenstein, G. O. R. A.; Pennings, A. J. *Br. Polym. J.* **1977**, *9*, 258.
(12) Smith, P.; Pennings, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 513.
(13) Wittmann, J. C.; Manley, R. St. J. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1089.
(14) Wittmann, J. C.; Manley, R. St. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1891.
(15) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1837, 1853.
(16) Wittmann, J. C.; Hodge, A. M.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2495.
(17) Dorset, D. L.; Pangborn, W. A.; Hancock, A. J. *J. Biochem. Biophys. Methods* **1983**, *8*, 29.
(18) Willems, J. *Naturwissenschaften* **1955**, *42*, 176.
(19) Moss, B.; Dorset, D. L.; Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1919.
(20) Dorset, D. L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 79.
(21) Dorset, D. L. *Biochim. Biophys. Acta* **1988**, *938*, 279.
(22) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 205.
(23) Teare, P. W. *Acta Crystallogr.* **1959**, *12*, 294.
(24) Dorset, D. L. *Acta Crystallogr.* **1976**, *A32*, 207.
(25) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504.
(26) Sinclair, V. C.; Robertson, J. M.; Mathieson, A. M. L. *Acta Crystallogr.* **1950**, *3*, 245, 251.
(27) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; pp 40–41, 108–110.
(28) Winchell, A. N. *The Optical Properties of Organic Compounds*; Academic Press: New York, 1954.
(29) Phillips, D. C.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1960**, *13*, 365.
(30) Miasnikova, R. M.; Kitaigorodskii, A. I. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1958**, *3*, 157.
(31) Sim, G. A.; Robertson, J. M.; Goodwin, T. H. *Acta Crystallogr.* **1955**, *8*, 157.
(32) Weast, R. C., Ed. *CRC Handbook of Chemistry Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1987; pp C724–726.
(33) Dollhopf, W.; Grossmann, H. P.; Leute, U. *Colloid Polym. Sci.* **1981**, *259*, 267.
(34) Dorset, D. L. *J. Electron Microsc. Tech.* **1987**, *7*, 35.
(35) Wendlandt, W. W. *Thermal Analysis*, 3rd ed.; Wiley: New York, 1986; p 276.
(36) Nyburg, S. C.; Potworowski, J. A. *Acta Crystallogr.* **1973**, *B29*, 347.
(37) Dorset, D. L. *J. Electron Microsc. Tech.* **1985**, *2*, 89.
(38) Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd rev. ed.; Pitzer, K. S., Brewer, L., Eds.; McGraw-Hill: New York, 1961; pp 227–230, 280–296.
(39) Lee, A. G. *Biochem. Biophys. Acta* **1978**, *507*, 433.
(40) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 507–511, 568–571.
(41) Kitaigorodsky, A. I. *Mixed Crystals*; Springer–Verlag: Berlin, 1984; pp 200 ff.
(42) Koynova, R. D.; Kuttenreich, H. L.; Tenchov, B. G.; Hinz, H.-J. *Biochemistry* **1988**, *27*, 4612.
(43) Dibrell, F. S.; Phillips, P. J. *Bull. Am. Phys. Soc.* **1988**, *33*(3), 589.
(44) Dorset, D. L. *Macromolecules* **1986**, *19*, 2965.
(45) Abrahamsson, S.; Dahlén, B.; Löfgren, H.; Pascher, I. *Prog. Chem. Fats Other Lipids* **1978**, *16*, 125.
(46) Sydow, E. v. *Ark. Kemi* **1956**, *9*, 231.
(47) Fryer, J. R. *J. Electron Microsc. Tech.*, in press.
(48) Dorset, D. L. *Acta Crystallogr.* **1980**, *A36*, 592.
(49) Dorset, D. L. *J. Electron Microsc. Tech.*, in press.
(50) Tammann, G. *A Text Book of Metallography*; Dean, R. G., Swenson, L. G., Translators, Chemical Catalog: New York, 1925; pp 178–179.

Kinetic–Mechanistic Studies on the Photorearrangement of *o*-Nitrobenzyl Ester Groups in Polymer Matrices

W. K. Wong,† H. Schupp,‡ and W. Schnabel*,†

Hahn-Meitner-Institut Berlin GmbH, Bereich Strahlenchemie, D-1000 Berlin 39, FRG, and BASF AG, D-6700 Ludwigshafen, FRG. *Received May 27, 1988*

ABSTRACT: Films of copolymers containing 5 mol % *o*-nitro-α-methylbenzyl acrylate and methyl methacrylate, butyl methacrylate, or butyl acrylate in various combinations were subjected to flash photolysis (λ_{inc} 347 or 355 nm; flash length, 25 ns or 100 ps, respectively) at temperatures between 77 and 473 K. Nitronic acid was formed as an intermediate at all temperatures via two routes: a very fast singlet route with a lifetime $\tau < 200$ ps and a "slow" triplet route conforming to first-order kinetics. The temperature dependence of both the nitronic acid yield and the rate constant of the slow formation process reflected changes in the physical state of the matrix connected with the onset of side group rotations and the glass transition. The decay of the nitronic acid groups was nonexponential at temperatures up to 450 K, i.e., even at temperatures above T_g. The decay of the optical density (OD) of nitronic acid conformed to the relationship $\text{OD}_t = \text{OD}_0 \exp(-\alpha t^{\beta})$ with $\beta = 0.5$. The kinetic matrix effect is discussed with respect to dispersive reaction kinetics and the free volume concept. At temperatures above 450 K, the nitronic acid decay followed first-order kinetics, indicating that local displacements and size variations of free volume elements were no longer the rate-determining process.

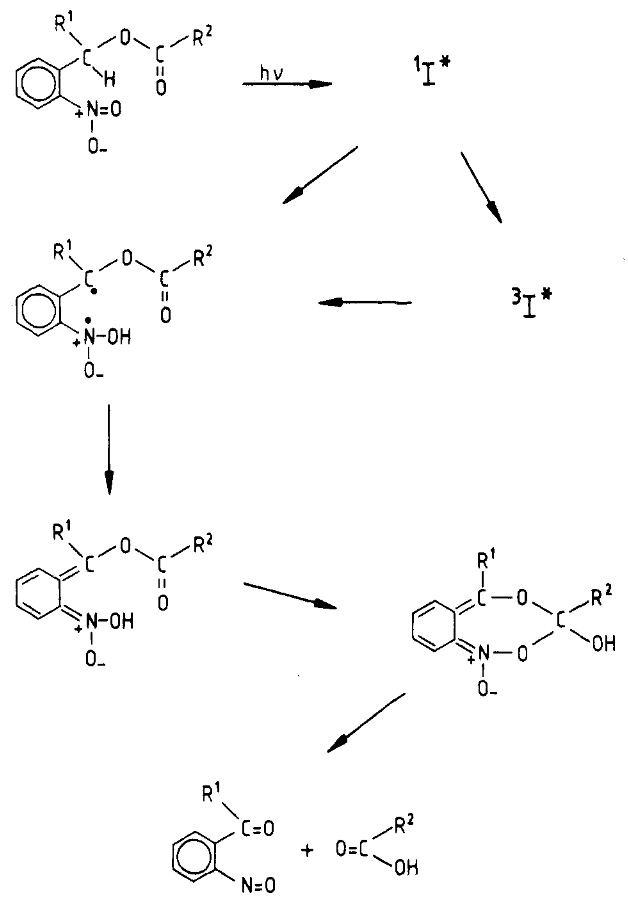
Introduction

The mechanism and the kinetics of the photorearrangement of *o*-nitrobenzyl esters in solution were the objective of recent studies,[1,2] which led to the mechanism illustrated in Scheme I. Notably, the rearrangement involves a rather long-lived intermediate, nitronic acid, which has a strong optical absorption band around $\lambda = 400$ nm. The quantum yields of bond cleavage in the photorearrangement, ϕ(PR), were found to be significantly influenced by the substituent R^1 in the α-position and to be

---

† Hahn-Meitner-Institut Berlin GmbH.
‡ BASF AG.

Scheme I
Mechanism of the Photorearrangement of *o*-Nitrobenzyl Esters



independent of the chemical nature of R^2 as far as R^2 = phenyl or isobutyl is concerned. Substitution of one of the α-hydrogens by methyl or phenyl increased ϕ(PR) from 0.1 to 0.2. The differences in ϕ(PR) corresponded to the differences in the yields of the nitronic acid intermediates.

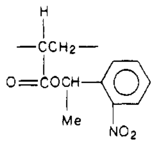
When copolymers of methyl methacrylate, acrylic acid esters of *o*-nitrobenzyl alcohol, and α-methyl-*o*-nitrobenzyl alcohol and moreover low molecular weight model compounds, such as α-methyl-*o*-nitrobenzyl benzoate and isobutyrate, were irradiated with UV light in dilute solution, a polymer effect with respect to the quantum yield was not detected. Also, a polymer effect concerning the kinetics of the formation and the decay of the nitronic acid intermediates could not be evidenced.

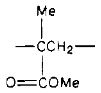
The present paper reports on results obtained with neat copolymers containing 5 mol % α-methyl-*o*-nitrobenzyl acrylate. The main objective of this work was to find out how physical transitions of the polymeric matrix affect the rearrangement depicted in Scheme I. Therefore, copolymers differing in matrix properties due to differences in chemical composition were examined, and formation and decay of nitronic acid were studied in a broad temperature range from 77 to 473 K.

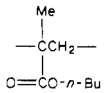
It will be shown that physical transitions were reflected both by the extent of nitroformic acid formation and by the formation kinetics. Striking differences between polymer films and polymer solutions were detected upon examining the decay of the nitroformic acid. With polymer films, a nonexponential decay of the nitronic acid was observed at temperatures between 170 and 450 K, indicating the existence of a kinetic matrix effect. In this connection, it is interesting to note that similar kinetic matrix effects were found by other authors upon investigating thermally induced intramolecular rearrangements or isomerizations of merocyanine compounds,[3-6] azo compounds,[7,8] and mercury dithiazonate[9] that were homogeneously dispersed in polymer matrices or chemically attached to the macromolecules forming the matrix.

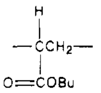
Table I
Composition of Copolymers Used in This Work

	1, mol %	2, mol %	3, mol %	4, mol %	M_w	T_g, °C
CP-1	5	60	35		8.5×10^4	74
CP-2	5	60	35		7.5×10^4	74
CP-4	5	95			1.1×10^5	103
CP-5	5	60		35	1.2×10^5	61


1


2


3


4

Experimental Section

Materials. Copolymers were synthesized by free-radical polymerization of monomer mixtures in ethyl acetate solution (50%) at 70–90 °C using AIBN (0.1 wt %) as initiator. At 30% conversion, the polymerization was interrupted, and the copolymer was precipitated with methanol and afterwards reprecipitated several times from ethyl acetate solution. The composition of the copolymers was determined by elemental analysis. The molecular weight was obtained from GPC measurements, and the glass transition temperature (T_g) was determined by differential scanning calorimetry. The copolymers used in this work are listed in Table I.

Preparation of Polymer Films. The copolymers were dissolved in 2-ethoxyethyl acetate at a concentration of 350 g/L. Quartz plates (Herasil, 75 × 15 × 1 mm) were coated with the polymer solution with the aid of an Erichson apparatus (Motorized Film Applicator, Model 509/1). The polymer-coated plates were kept, at first, for 3 h at 0.1 Torr and at room temperature and then for 3 h at 100–125 °C. Subsequently, they were stored for 2–3 days in vacuo. The film thickness was between 30 and 35 μm, as measured by a digital micrometer (Sviluppo Tecnologie Avanzate). For a given film, the thickness varied by ±5% (controlled by absorption measurements).

Irradiation of Polymer Films. The irradiations were performed at temperatures between 77 and 473 K in a cryostat (Oxford Instruments, Model DN 1704). After insertion of a sample plate, the cryostat was evacuated to 10^{-5}–10^{-6} Torr for 3 h. Prior to irradiation, it was filled with O_2-free argon. With the aid of a vacuum passage device (Balzers, rotary linear motion feed through DN40KF), the plate could be moved up and down, thus allowing the irradiation of six different sections of the film. Both the photolyzing and the analyzing light beams were incident on the film at angles of 45°.

For the 25-ns flash photolysis at λ_{inc} = 347 nm, a ruby laser (Korad, Model K1QS2) was used in conjunction with a ADP frequency doubler. For the 100-ps flash photolysis at λ_{inc} = 355 nm, a Nd-YAG laser system (J. K. Lasers, Model AML) was used in conjunction with a KD_2PO_4 frequency tripler. In this case, a photodiode (Type F-4014, ITT, Fort Wayne, IN) was used for optical absorption measurements. The output signals were digitized with the aid of a transient recorder (Tectronix R 7912) and stored and evaluated in a microcomputer.

Actinometry. PMMA films containing (*E*)-(α-(2,5-dimethyl-3-furyl)ethylidene)isopropylidenesuccinic anhydride (Aberchrome 540, Aberchromics Ltd.) were irradiated and the absorbed dose was calculated from the OD at 494 nm formed during the flash ($\epsilon_{494nm} = 7.8 \times 10^3$ L/(mol cm), ϕ = 0.2). Films that were 55 μm thick containing about 8 wt % Aberchrome 540 were prepared from an ethyl acetate solution containing PMMA (147 g/L) and Aberchrome 540 (11.7 g/L).

Results

Changes in Ground-State Absorption Spectra. As can be seen from Figure 1, the ground-state absorption

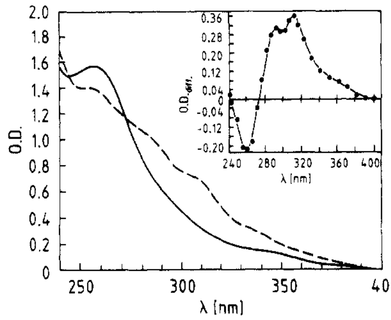


Figure 1. Light-induced changes in the ground-state absorption spectrum of copolymer CP-5. Film thickness: 33 μm. The film was irradiated with 30 flashes at λ_{inc} = 347 nm. $D_{abs} = 2 \times 10^{-5}$ einstein/(L flash). (—) Unirradiated film. (---) Irradiated film.

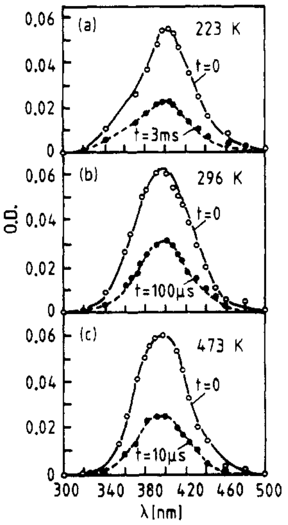


Figure 2. Transient absorption spectra recorded with a film of copolymer CP-1 (d = 32 μm) at the end of the 25-ns flash (t = 0) and after a certain time, as given in the graphs. λ_{inc} = 347 nm. $D_{abs} = 1.5 \times 10^{-5}$ einstein/(L flash). Temperature: 223 K (a), 296 K (b), 473 K (c).

spectrum changed significantly on irradiating a film of CP-5 at λ_{inc} = 347 nm. Similar spectral changes were observed with the other copolymers. The difference spectrum with peaks at 290 and 310 nm shown in the inset of Figure 1 is very similar to the spectrum of nitrosobenzene in this wavelength range. Nitrosobenzene exhibits absorption maxima at 282 and 306 nm in acetonitrile solution. The changes in the OD caused by irradiation of the copolymer films are, therefore, attributed to the formation of nitrosobenzene groups.

Transient Absorption Spectra. At all temperatures (77–473 K), a broad absorption band with a maximum at about 400 nm was formed during the 25-ns flash (λ_{inc} = 347 nm). Typical transient spectra recorded with a film of CP-1 are shown in Figure 2. Quite similar spectra were observed with the other copolymers. The spectra decayed without changing shape. They are identical with the transient absorption spectra recorded with the copolymers and with model compounds in dilute solution and are attributed to "nitronic acid".

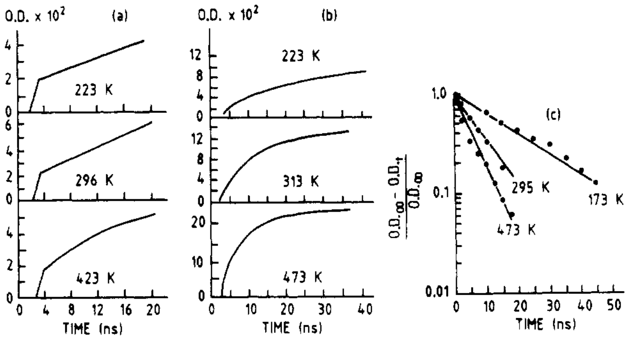


Figure 3. Formation of nitronic acid in films of copolymer CP-1 (d = 34 μm) at various temperatures (given in the graphs). Increase in the optical density recorded at 410 nm after the 100-ps flash (λ_{inc} = 355 nm) with high (a) and medium (b) time resolution. First-order plots of the increase in the OD are presented in (c). $D_{abs} = 5.5 \times 10^{-6}$ einstein/(L flash).

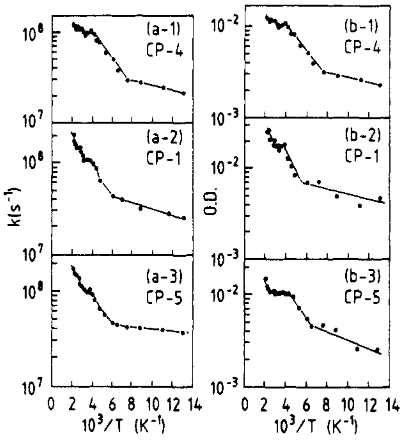


Figure 4. Formation of nitronic acid in copolymer CP-1, CP-4, and CP-5. Arrhenius plots of the first-order rate constants of the slow formation process (a-1–a-3) and of the maximum of the optical density of the nitronic acid formed after the flash (b-1–b-3).

Table II
Transient Optical Density at 410 nm Formed at Constant Absorbed Dose in Copolymer CP-1

temp, K	OD_{fast}[a]	OD_{∞}[b]	f_{fast}[c]
77	2.0×10^{-2}	4.3×10^{-2}	0.47
173	2.0×10^{-2}	7.0×10^{-2}	0.29
223	2.0×10^{-2}	9.0×10^{-2}	0.22
313	2.0×10^{-2}	13.0×10^{-2}	0.15
473	2.0×10^{-2}	24.0×10^{-2}	0.08

[a] OD formed at t < 200 ps. [b] Maximum OD formed after the flash. [c] Fraction of rapid buildup.

Table III
Temperatures (K) That Apply to the Discontinuities in the Arrhenius Plots of *k* and OD (Refer to Figure 4). For Comparison, Relaxation Temperatures of PMMA Are Given

polymer[a]			relaxation	
CP-1	CP-4	CP-5	range[b]	remarks
347 (348)	376 (376)	334 (334)	374–390	glass transition, onset of segmental motions
256	256	256	240–270	onset of motions of ester groups
167	147	169	150–170	onset of motions of α-methyl groups

[a] Measured T_g values in parentheses. [b] References 9–11.

Formation of Nitronic Acid. Upon irradiating polymer films with 100-ps flashes (λ_{inc} = 355 nm), it was found that the buildup of the absorption of the nitronic acid occurred in two modes. This is shown in Figure 3a for polymer CP-1. Analogous results were obtained with the other polymers. Actually, the rapid mode of the buildup could not be time-resolved. It was faster than the time constant of the setup (ca. 200 ps). Notably, at constant absorbed dose, the yield of the rapidly formed transient was the same at all temperatures as is demonstrated in Table II. The slow process (see Figure 3b) conformed to

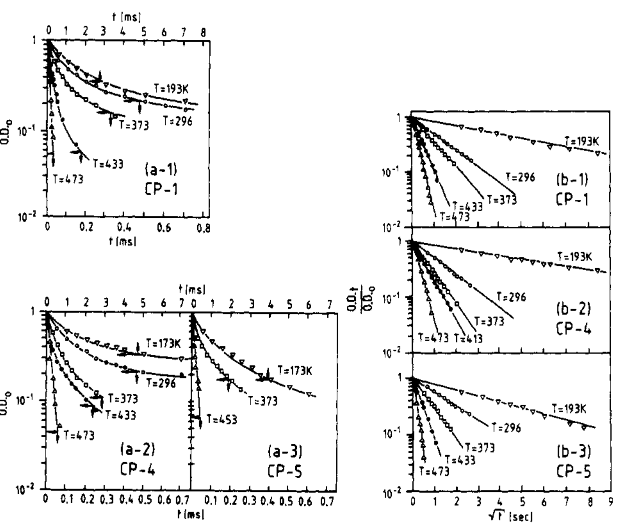


Figure 5. Decay of nitronic acid in copolymers CP-1, CP-4, and CP-5 at various temperatures as indicated in the graphs. log OD_t/OD_0 versus the time (a) and versus the square root of the time (b).

first order kinetics. Typical first-order plots are shown in Figure 3c. Arrhenius plots of the first-order rate constant, k, pertaining to the "slow" formation process are shown in parts a-1–a-3 of Figure 4. Obviously, the temperature dependence of k does not comply with a relationship of the form of the Arrhenius equation $k = k_0 \exp(-E_A/RT)$. From Table III it can be seen that the temperatures that apply to the discontinuities in the function $k = f(1/T)$ reflect relaxation temperature ranges reported for PMMA in the literature.[9-11] These relaxation temperatures correspond to the glass transition (376 K), the onset of the rotation of ester groups (240–270 K), and the onset of the rotation of α-methyl groups (150–170 K). It can be seen from Figure 4b-1–b-3 that the temperature dependence of the yield of nitronic acid, expressed here by the maximum optical density at λ = 400 nm, formed after the flash, is quite similar to that of the buildup rate constant.

According to the reaction mechanism presented in Scheme I, nitronic acid can be formed, apart from the singlet route, also via the triplet route. We were, therefore, interested to evidence the triplet state of *o*-nitrobenzyl esters. In this connection, it is notable that Yip et al.[13,14] reported absorption spectra of triplets of *o*-nitrobenzyl compounds with a maximum around 550 nm. As a matter of fact, a short-lived absorption band around 600 nm (τ is less than or equal to a few nanoseconds) was detected on irradiating the copolymer films. Unfortunately, we were not able to determine the decay rate because of a rather intense emission or scattering signal which disturbed our measurements.

Decay of Nitronic Acid. The spectrum of the nitronic acid decayed in the microsecond range without changing its shape. It can be seen from Figure 5a-1–a-3 that, apart from rather high temperatures, the decay was nonexponential. This contrasts the decay kinetics observed with the same polymers in fluid media at room temperature.[1] In this case, the decay was clearly first order. The different behavior found for the decay in the solid polymers indicates the occurrence of a "kinetic matrix effect" similar to that found by other authors with indolinobenzospiranes and other photochromic systems.[3-8] Also in those cases, the kinetic matrix effect was manifested by nonexponential decay kinetics. A further analogy to the other cases was found in the present work: semilogarithmic plots of the normalized OD of the nitronic acid versus the square root of the time yielded straight lines. This is shown in Figure 5b-1–b-3. Actually, the decay of the optical density of the nitronic acid conforms to the kinetic relationship

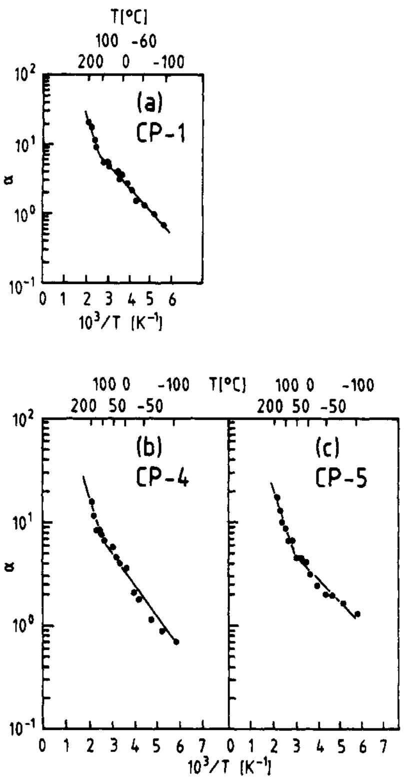


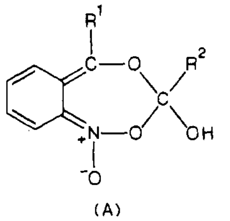
Figure 6. Arrhenius plots of the matrix response function time constant α based on data obtained with copolymers CP-1 (a), CP-4 (b), and CP-5 (c).

$$OD_t/OD_0 = e^{-\alpha t^{\beta}} \tag{1}$$

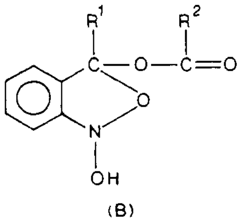
with β = 0.5. An Arrhenius plot of the matrix response function time constant, α, is shown in Figure 6, where one can see that in all cases a significant discontinuity of the function $\alpha = f(1/T)$ exists at temperatures corresponding to the glass transition.

Discussion

Mechanism. From the results reported in this paper, it is inferred that, in solid polymer films, the mechanism of formation and decay of the nitronic acid intermediate is the same as in solution. Therefore, the discussion of the results is based on the mechanism presented in Scheme I. With respect to earlier work, this mechanism has been subject to modification as far as the decay of the nitronic acid is concerned. Since the transient absorption spectrum is not changing its shape during the decay, it seems that the *o*-quinone structure is maintained during the decay, although an additional intermedite is very probably formed. It has indeed been evidenced in aqueous solution of appropriate water-soluble copolymers by changes in the electrical conductivity.[1] Therefore, it is now proposed that the structure of this intermediate is A rather than B.



(A)



(B)

Formation of Nitronic Acid. Regarding the assignment of the two buildup processes of the transient absorption ($\lambda_{max} \approx 400$ nm), two cases were discussed earlier:[1] (1) The two modes reflect the existence of two different species, the decay of the short-lived one giving rise to the formation of the long-lived one. (2) Nitronic acid is formed via two routes, the singlet and the triplet route.

In this work it was found that the extent of the OD formed by the rapid and the slow processes, respectively, depended in quite different manners on the temperature: whereas the extent of the rapidly formed OD did not depend on the temperature, the extent of the slowly formed OD increased with increasing temperature. From these findings it is inferred that case 2 is applicable to our system. The high formation rate of the rapid mode ($\tau < 200$ ps) is in accordance with a very short singlet lifetime. Consequently, nitronic acid formation via the singlet route is restricted to those molecules that are excited in a conformational state having α-hydrogens and nitro groups located at reaction distance. Triplets are significantly longer-lived than singlets. Therefore, the yield of nitronic acid formed via triplets can increase with increasing temperature because conformational changes due to intramolecular motions provide for an approach of the reaction sites.

Actually, the formation of nitronic acid is an intramolecular hydrogen-transfer process which could principally be based on hydrogen tunneling. Hydrogen-tunneling mechanisms have been proposed in connection with intramolecular H-transfer processes,[15,16] e.g., the enol → keto transition of 2-methylacetophenone. In these cases, hydrogen tunneling was evidenced, in accord with results from theoretical treatments[17] by the temperature dependence of the rate constant, k, according to

$$k = k^0 \exp(CT) \tag{2}$$

where C is a constant, and by a deuterium isotope effect on k, exceeding in extent the usual kinetic isotope effects.

In the present work, the occurrence of an isotope effect could not be examined because deuterated compounds were not available. For the slow buildup process, a temperature dependence of k according to eq 2 was found for the temperature range $T < 200$ K. At higher temperatures, k was strongly determined by changes in the mobility of the matrix as can be seen from Figure 4 and Table II, which show that the discontinuities in the Arrhenius plots of k are related to the relaxation temperatures of the matrix.

It is interesting to note that, in contrast to the decay of the nitronic acid, a kinetic matrix effect was not observed for the slow mode of the buildup of the transient absorption. In other words, the slow formation process conformed with first-order kinetics at all temperatures. This result indicates that the activation volume of the formation process must be very small.

In conclusion, the yield of the nitronic acid is essentially determined by the extent to which triplets can undergo intramolecular H abstraction. This process is favored by an increase in the "matrix mobility", which relies on the capability of the side groups (methyl, ester, etc.) to rotate. Triplet-excited o-nitrobenzyl groups that cannot attain a conformational state favoring internal H abstraction during their lifetime will be deactivated nonchemically, i.e., they will "return" to the ground state.

Decay of Nitronic Acid. It is interesting to note that, over a broad temperature range, the decay of nitronic acid groups in polymer films is clearly nonexponential, whereas the formation, at least as far as the slow mode is concerned, is exponential. That we are dealing here with a polymer matrix effect becomes obvious from Figure 7, where the decay in film and in dilute solution is compared. In solution, the decay is exponential. Nonexponential decay kinetics have recently been the objective of intense research by Richert and Bässler[18-20] in connection with the merocyanine → spiropyran transformation. According to these authors, nonexponential kinetics of rearrangements can be quite generally interpreted on the basis of the concept of "dispersive reaction kinetics" which was eleborated by Siebrand and Wildman.[21] The dispersion is assumed to arise from random variations of the energy barrier controlling the molecular motion. Moreover, it is assumed that "*the individual decay rate is thermally activated and that the individual barrier heights are subject to a Gaussian distribution centered around a mean value* $\Delta\epsilon_0$ *with a standard deviation* σ". When appropriate parameter values are chosen, experimental curves were fitted, and for conversions exceeding about 10%, the decay kinetics followed a law according to eq 1 with $\beta = 0.37$–0.40, depending on temperature.[18] These values are of similar order as $\beta = 0.5$ found in this work. While the importance of this quite formal treatment for the kinetics of the decay of nitronic acid is investigated at present in our laboratory, the application of a physical model, namely, the so-called "*free volume concept*" (see, for example, ref 3), seems still to be attractive with respect of the interpretation of the results obtained in this work. Following the lines of the free volume concept, nitronic acid groups can rearrange to form the final products only if enough "free volume" is available in their immediate neighborhood. The critical condition for the rearrangement is

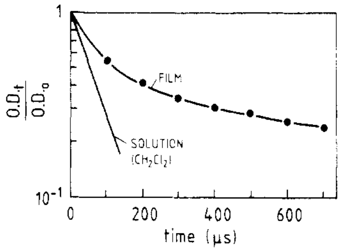


Figure 7. First-order plots of the decay of the optical density of nitronic acid groups at $\lambda_{inc} = 400$ nm and at $T = 298$ K in film and in dilute CH_2Cl_2 solution (1.5 g/L).

$$v_f \geq v_a \tag{3}$$

v_f is the volume of the free volume element; v_a is the activation volume. v_a must be much larger for the second step of the rearrangement (decay of nitronic acid) than for the first step (formation of nitronic acid). If condition 3 is fulfilled, the rearrangement occurs immediately. It must be considered that there is a local and a size distribution of v_f, both of which are subject to variation as time proceeds. The driving force for this change derives from the rotational motions of side groups. The motions provide not only for changes in size, i.e., expansion or collapse, but also for local displacements of free volume elements. Consequently, both "diffusion" and "size variations" of free volume elements are involved in the decay of nitronic acid. The rate of these processes determines the total rate of the nitronic acid decay as long as they are slower than the chemical step. This becomes quite obvious if one realizes that the kinetic matrix effect is still operative at temperatures exceeding the glass transition range. Only at $T > 450$ K were exponential decay kinetics observed, indicating that, here, the mobility of free volume elements is high and, therefore, no longer determines the rate of the second step of the rearrangement.

Acknowledgment. The authors are very grateful to the late Dr. G. Beck for maintaining the flash photolysis set ups and for very valuable advice. Moreover, the help of

Macromolecules 1989, *22*, 2181–2186

Dr. J. Lilie and Dr. E. Janata regarding the computer evaluation of data and the maintenance of the signal detection system, respectively, was highly appreciated.

Registry No. CP-1, 107137-72-4; CP-4, 116461-92-8; CP-5, 116461-93-9.

References and Notes

(1) Schupp, H.; Wong, W. K.; Schnabel, W. *J. Photochem.* **1987**, *36*, 85.

(2) Zhu, Q. Q.; Schnabel, W.; Schupp, H. *J. Photochem.* **1987**, 39, 317.

(3) Kryszewski, M.; Nadolski, B.; North, A. M.; Pethrick, R. A. *J. Chem. Soc. Faraday Trans. 2* **1980**, *76A*, 351.

(4) Kryszewski, M.; Lapienis, D.; Nadolski, B. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2423.

(5) Vandewijer, P. H.; Smets, G. *J. Polym. Sci., Part C* **1968**, *22*, 231.

(6) Horie, K.; Tsukamoto, M.; Mita, I. *Eur. Polym. J.* **1985**, *21*, 805. Mita, I.; Horie, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27*, 91.

(7) Priest, W. J.; Sifain, M. M. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 3161.

(8) Chernayakovskii, F.; Chernayakovskii, K.; Blumenfeld, L. *J. Phys. Chem. (Moscow)* **1973**, *47*, 5.

(9) Kryszewski, M.; Nadolski, B.; Fabrycy, A. *Rocz. Chem.* **1975**, *49*, 2077.

(10) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; Chapter V.

(11) Kolarik, J. *Adv. Polym. Sci.* **1982**, *46*, 119.

(12) Robert, G. E.; White, E. F. T. In *The Physics of Glassy Polymers*; Haward, R. N., Ed.; Applied Science: London, 1973.

(13) Yip, R. W.; Sharma, D. K.; Giasson, R.; Gravel, D. *J. Phys. Chem.* **1984**, *88*, 5770.

(14) Yip, R. W.; Sharma, D. K.; Giasson, R.; Gravel, D. *J. Phys. Chem.* **1985**, *89*, 5328.

(15) Grellmann, K.-H.; Weller, H.; Tauer, E. *Chem. Phys. Lett.* **1983**, *95*, 195.

(16) Grellmann, K.-H.; Schmitt, U.; Weller, H. *Chem. Phys. Lett.* **1982**, *88*, 40.

(17) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4083, 4089.

(18) Richert, R.; Bässler, H. *Chem. Phys. Lett.* **1985**, *116*, 302.

(19) Richert, R. *Chem. Phys. Lett.* **1985**, *118*, 534.

(20) Richert, R.; Elschner, A.; Bässler, H. *Z. Phys. Chem. N.F. (Munich)* **1986**, *149*, 63.

(21) Siebrand, W.; Wildman, T. A. *Acc. Chem. Res.* **1985**, *19*, 238.

Molecular Weight and Tacticity Fractionations in Successive Extraction of Highly Isotactic Polypropylene with *n*-Alkane Solvents

Hidetoshi Kawamura

Polymer Development Laboratory, Tokuyama Soda Co. Ltd., 1-1, Harumichou, Tokuyama 745, Japan

Tetsuo Hayashi, Yoshio Inoue,* and Riichirô Chûjô

Department of Polymer Chemistry, Tokyo Institute of Technology, 12-1, O-okayama 2-chome, Meguro-ku, Tokyo 152, Japan.

Received May 23, 1988; Revised Manuscript Received October 7, 1988

ABSTRACT: The highly isotactic polypropylene prepared with a δ-$TiCl_3/Et_2AlCl$ catalytic system was fractionated by successive extraction with *n*-alkane solvents. The pentad tacticities in the respective fractions and the whole polymer were determined from the ^{13}C NMR spectra. A mechanism of stereospecific polymerization was statistically analyzed from the values of pentad tacticities on the basis of the two-site model, in which at one site (APP site) polymerization proceeds according to the Bernoullian model of selection between meso and racemo configurations and at the other site (IPP site) according to selection between dextro and levo. Further, molecular weights of the respective fractions and the whole polymer were measured. From these results, it was indicated that both molecular weight and tacticity fractionations occur for the isotactic polymer produced at the IPP site and molecular weight fractionation mainly occurs for the atactic polymer produced at the APP site in the successive extraction. Also indicated was that the number-average molecular weight of the isotactic polymer is much larger than that of the atactic polymer. This suggests that the ratio rate of the propylene propagation reaction/rate of the chain transfer reaction at the IPP site is much larger than that at the APP site.

Introduction

Polypropylenes having high crystallinity can be prepared with stereospecific Ziegler–Natta catalytic systems. It is well-known that the less crystalline polymer can be removed by a suitable extraction. It is possible to isolate fractions having different melting points (106–175 °C) and crystallinities (15–66%) by the extractions with different *n*-alkane solvents.[1] Nakajima et al.[2] fractionated polypropylene by extraction with boiling hydrocarbons with different boiling points and confirmed that the respective polymer fractions have different molecular weights and isotacticities. Their results suggest that the tacticity and molecular weight fractionations occur in the *n*-alkane extraction. Further, it has been confirmed that the respective fractions obtained with the successive extraction of polypropylenes with boiling *n*-alkane solvents have different pentad tacticities,[3-5] indicating the occurrence of the tacticity fractionation. On the basis of these previous results, Kissin[6] considered the continuous distribution of active centers with different stereoregularity.

The mechanism of stereospecific polymerization has been statistically analyzed from the values of tacticities in polypropylenes prepared with various Ziegler–Natta catalytic systems.[7-16] It has been concluded that neither Bernoullian[10] nor first-order Markovian[11] statistical models describe the polymerization mechanism of propylene except the syndiotactic sample prepared with a VCl_4–$Al(CH_3)_2Cl$–anisole catalytic system, which obeys Bernoullian statistics (polymerization proceeds through the selection between meso (*m*) and racemo (*r*)).[13] Zambelli et al.[13] and Chûjô[14] proposed the two-site model for the mechanism of propylene polymerization, in which at one site polymerization proceeds according to the Bernoullian model of selection between meso and racemo configurations (symmetric model) and at the other site (IPP site) according to selection between dextro (*d*) and levo (*l*) (asymmetric

0024-9297/89/2222-2181$01.50/0 © 1989 American Chemical Society