High Molecular Weight Anthracene Containing Polymer

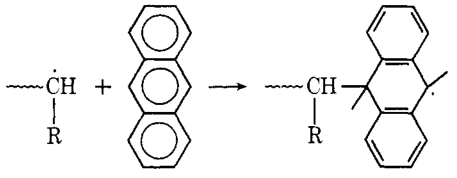
Milan Štolka

Polymer Physics and Chemistry Area, Xerographic Technology Department, Xerox Corporation, Webster, New York 14580.

Received September 6, 1974

ABSTRACT: An anthracene group containing monomer, 1-(2-anthryl)ethyl methacrylate (I) (mp 161°), was synthesized by condensation of 1-(2-anthryl)ethanol with methacryloyl chloride (yield, 95%). I was polymerized by a free-radical mechanism to a soluble linear amorphous polymer with $\bar{M}_w$ up to 280,000 (MWD = 2.7). I was also copolymerized with methyl methacrylate (II) and dodecyl methacrylate. Copolymerizations of I (21.8 mol %) and II (78.2 mol %) in xylene at 70° initiated with benzoyl peroxide run to 45% conversion gave product with 31.6 mol % of I: $\bar{M}_w$ = 530,000; MWD = 3.3. I inhibited polymerization of *N*-vinylcarbazole and vinyl acetate.

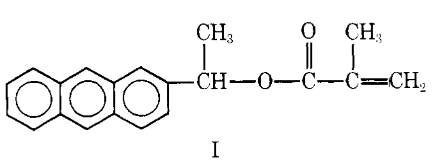
The synthesis of polymers with anthracene groups has been attempted many times. The reason for failure to achieve this goal by radical addition polymerization is that the anthracene group itself is an efficient radical quencher and inhibitor of radical polymerizations. The propagating macroradicals are presumably stabilized by formation of unreactive dibenzylic radicals by direct addition of anthracene.



The extreme reactivity of the anthracene group toward free radicals made it impossible to synthesize for example a high molecular weight polymer of 9-vinyl anthracene.[1]

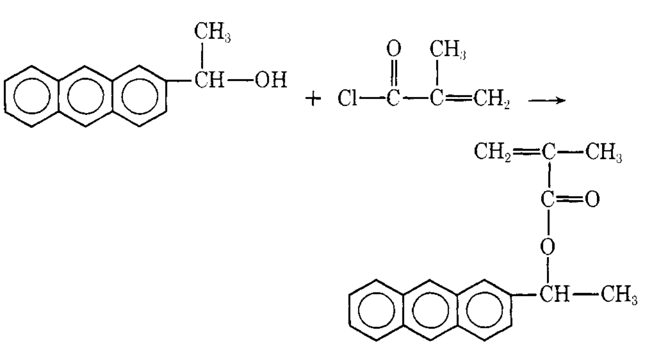
However, anthracene does not interfere with the radical polymerization of methyl methacrylate,[2] at least in the absence of uv radiation. The light-induced polymerization of methyl methacrylate at 40° in the presence of benzoyl peroxide is also inhibited by anthracene.[3] In the darkness, neither addition of anthracene to the methyl methacrylate macroradical nor chain transfers have been observed.

We assumed that the methacrylate group attached to anthracene by a covalent bond should be polymerizable. To prove that this assumption was correct we synthesized an anthracene-containing ester of methacrylic acid, 1-(2-anthryl)ethyl methacrylate (2AEMA), and studied its polymerization.



I

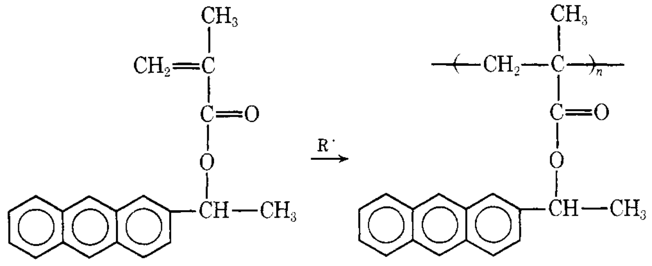
The monomer was synthesized by condensation of 1-(2-anthryl)ethanol with methacryloyl chloride.



In a typical synthesis, 11.0 g (4.96 × 10^{-2} mol) of the alcohol[4] was dissolved in 75 ml of dioxane at 70° in the presence of 7.5 ml of triethylamine. To this solution, 5.5 ml (5.6 × 10^{-2} mol) of freshly distilled methacryloyl chloride was added and the mixture was heated for 24 hr. The product was isolated in water, filtered, washed, dried, and recrystallized from benzene–methanol: yield, 9.3 g (3.2 × 10^{-2} mol, 65%) of white 2AEMA; mp 161°.

Anal. Calcd: C, 82.73; H, 6.25; O, 11.02. Found: C, 82.84; H, 6.25; O, 11.09.

The monomer was polymerized in common solvents such as benzene, xylene, dimethylformamide, and dioxane using initiators such as benzoyl peroxide, azobis(isobutyronitrile) and di-*tert*-butyl peroxide.



In a typical experiment, 3.0 g of 2AEMA was polymerized in 30 ml of benzene in nitrogen atmosphere using 0.02 g of azobis(isobutyronitrile) at 67° for 24 hr. The system was protected against light. The yield, after reprecipitation from benzene in acetone, was 2.8 g (93%). The polymer is soluble in benzene, xylene, methylene chloride, chloroform, tetrahydrofuran, dimethylformamide, 1,1,2,2-tetrachloroethane, and *o*-dichlorobenzene. No insoluble polymer was formed.

The average molecular weight was determined by membrane osmometry (in *o*-dichlorobenzene) ($\bar{M}_n$ 102,000) and light scattering ($\bar{M}_w$ 280,000) using tetrahydrofuran as a solvent. The molecular weight distribution factor of 2.74 was confirmed by gpc. The polymer obtained by radical polymerization is amorphous; no crystallinity was detected even in annealed samples. The complete solubility of the polymer and the similarity of the infrared spectra of the monomer and the polymer, particularly in the range of the aromatic-ring associated absorptions at 670–750 cm^{-1} (Figure 1), indicated that the polymer structure is that of a linear acrylic type not complicated by across-the-ring additions such as in cationically polymerized 9-vinyl anthracene.[5]

The uv spectrum of the polymer (in THF) shows typical anthracene absorptions at λ_{max} 313, 328, 345, 362, and 382 nm. The proton nmr spectrum (Figure 2) shows a broad diffused signal at τ 4.5 which is in the same region as shielded aromatic protons in poly(*N*-vinylcarbazole) and

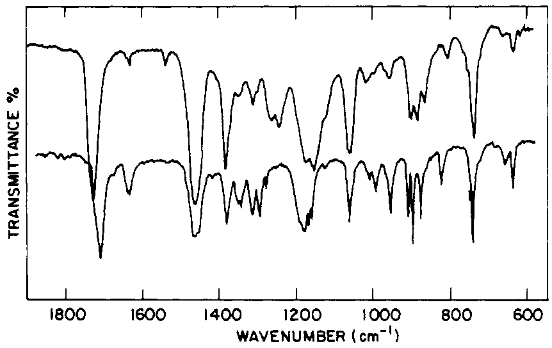


Figure 1. Infrared spectrum of poly(2AEMA) (upper curve) and 2AEMA (lower curve) in Nujol.

poly(*N*-ethyl-2-vinylcarbazole).[6] A relationship between the degree of shielding and electronic mobilities has been proposed.[6] From the spectrum it appears that poly(1-(2-anthryl)ethyl methacrylate) also exhibits large shielding of one or more aromatic protons.

As anticipated, 1-(2-anthryl)ethyl methacrylate can be copolymerized with other esters of methacrylic acid such as methyl methacrylate (MMA) and dodecyl methacrylate.

For example, 1.0 g (3.5×10^{-3} mol) of 2AEMA and 1.25 g (12.5×10^{-3} mol) of MMA were copolymerized in 10 ml of xylene at 70° for 20 hr using 0.01 g of benzoyl peroxide as an initiator. The yield was 1.0 g; the percentage composition of 2AEMA units in the copolymer, as determined by the elemental analysis, was 31.6 mol %: $\bar{M}_w = 530{,}000$; $\bar{M}_w/\bar{M}_n = 3.3$. On the other hand, 2AEMA did not copolymerize with, and even inhibited the homopolymerization of, *N*-vinylcarbazole and vinyl acetate. Thus, by utilizing the unique nonreactivity of the electron defficient methacrylate radical toward anthracene we have been able to synthesize a high molecular weight anthracene-containing polymer. The physical properties of the polymer are under investigation.

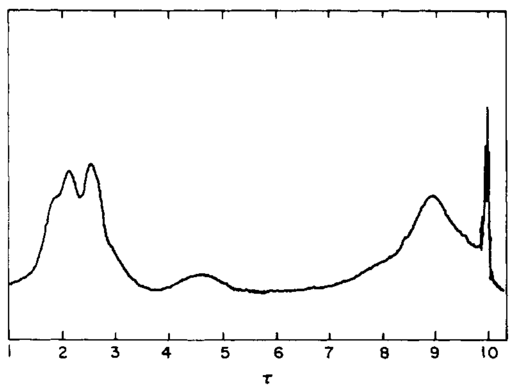


Figure 2. Proton nmr spectrum (60 MHz) of poly(2AEMA) at room temperature in $CDCl_3$.

References and Notes

(1) A. Rembaum and A. Eisenberg, *Macromol. Rev.*, **1**, 57 (1967).
(2) K. S. Bagdasaryan and A. A. Sinitsyna, *J. Polym. Sci.*, **52**, 31 (1961).
(3) T. Ya. Smirnova, G. P. Gladyshev, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, **170**, 118 (1966).
(4) A. Etienne, G. Arditti, and A. Chmelevsky, *Bull. Soc. Chim. Fr.*, 669 (1965).
(5) R. H. Michel, *J. Polym. Sci. Part A*, **2**, 2533 (1964).
(6) W. W. Limburg and D. J. Williams, *Macromolecules*, **6**, 787 (1973).

On the Kinetics of Polymer Degradation in Solution. II. Laser Flash Photolysis Studies on Poly(phenyl vinyl ketone) and Butyrophenone

G. Beck, G. Dobrowolski, J. Kiwi, and W. Schnabel*

Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, 1 Berlin 39, Germany. *Received October 4, 1974*

ABSTRACT: Using the nanosecond flash photolysis technique transient absorption spectra of poly(phenyl vinyl ketone) (PPVK) and butyrophenone (BP) in benzene solution at room temperature were recorded. Samples were irradiated with 347.1-nm light flashes. With both substances the transient spectra decayed by a first-order process with $k_1 = 1.0 \pm 0.2 \times 10^7$ sec^{-1}. In PPVK and BP solutions containing naphthalene or biphenyl the established triplet absorption of these compounds is sensitized. It is concluded that the observed transient absorptions are due to triplet states of PPVK and BP, respectively. The quencher studies yielded as an estimate a triplet quantum yield $\phi(^3\mathrm{PPVK}^*)$ equal to 0.1 to 0.3. k_Q (bimolecular rate constant of energy transfer) is about two times smaller for biphenyl than for naphthalene. For BP k_Q is about two and a half times higher than for PPVK (in the case of naphthalene: $k_Q(\mathrm{BP}) = 5.0 \pm 1.5 \times 10^9\ M^{-1}$ sec^{-1} and $k_Q(\mathrm{PPVK}) = 2 \pm 1 \times 10^9\ M^{-1}$ sec^{-1}). This result reflects the influence of the diffusion constant of the polymer on k_Q as expected for diffusion-controlled reaction and agrees with earlier findings[10] concerning rate constants of the reaction of scavengers with macroradicals.

I. Introduction

We reported recently[1] on time-resolved measurements of main chain scissions in poly(phenyl vinyl ketone) (PPVK) in benzene solutions. The scissions were induced by flashes from a ruby laser (λ 347 nm, half-width 25 nsec) and were monitored by the light-scattering detection method. During these investigations it was found that the light-scattering intensity decreased after the flash with a half-life of about 20 μsec. The interpretation of this result involved the question of how fast the scission of a C–C bond in the main chain of PPVK is accomplished. This work concerns kinetic investigations on these questions using the same equipment as before. At present it appears to be well established[2-4] that bond fractures in PPVK occur *via* base units excited in their triplet states. Therefore, the optical detection method was applied in order to follow the kinetics of triplet decay by observing triplet–triplet absorption and intermolecular energy transfer between excited PPVK molecules and quenchers such as naphthalene and certain dienes.

Analogous experiments were carried out with butyrophe-