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Reaction of Acenaphthylene with the Benzoyloxy Radical

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ABSTRACT

Acenaphthylene (ACN) has been polymerized at 60°C using benzoyl peroxide labeled with carbon-14 and tritium as the initiator. End-group analyses show a very high proportion of benzoate groups among the incorporated initiator fragments. It is deduced that ACN is much more reactive than most other monomers toward the benzoyloxy radical. There is evidence that transfer to benzoyl peroxide is significant during the polymerization of ACN.

Acenaphthylene (ACN) polymerizes readily by radical and ionic mechanisms because conversion of the double bond in the monomer to a single bond in the polymer relieves some of the considerable strain in the five-membered ring [1]. The value of the monomer reactivity ratios for radical copolymerizations involving ACN show that the monomer is very reactive toward polymer radicals of various types;

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it also has high reactivity toward the 2-cyano-2-propyl radical derived from azobis(isobutyronitrile) (AIBN) [2]. We now report a study of the polymerization of ACN using benzoyl peroxide (BPO) as initiator, based upon examination of the endgroups derived from the initiator and designed to give information on the reactivity of the monomer toward the benzoyloxy radical.

Preliminary experiments were performed using benzoyl-carbonyl-^{13}C-peroxide (^{13}C-BPO) as initiator for copolymerizations of ACN with methyl methacrylate (MMA). Although the benzoate endgroups in the two homopolymers gave ^{13}C-NMR signals with different chemical shifts, it was not possible to distinguish between benzoate groups attached to the two types of monomeric unit in copolymers. As reported already [2] for the case of styrene with MMA, ^{13}C-BPO cannot at present be used in the same way as ^{13}C-AIBN to compare reactivities of monomers toward primary radicals.

It was necessary to revert to an established procedure [3] involving determination of the relative numbers of benzoate and phenyl endgroups in homopolymers prepared using BPO as thermal initiator. The results can be used to find the ratio of the velocity constants for the competing reactions

$$C_6H_5.CO.O. \longrightarrow C_6H_5. + CO_2 \qquad (1)$$

$$C_6H_5.CO.O. + M \longrightarrow C_6H_5CO.O.M. \qquad (2)$$

Values of k_2 for various monomers can then be compared using Reaction (1) for reference.

The most convenient procedure for comparison of the number of benzoate and phenyl endgroups requires the use of BPO labeled with carbon-14 in the carbonyl groups and tritium in the benzene rings (^{14}C-^{3}H-BPO) so that the benzoate endgroups are doubly labeled whereas the phenyl endgroups are labeled with tritium only; the general method of working has been described [4]. The average molecule in a sample of a polymer prepared with BPO as initiator can be represented as

$$(C_6H_5.CO.O)_x(C_6H_5)_{1-x}(M)_n \qquad (3)$$

Suppose that c and C are the disintegration rates for carbon-14 per unit mass of polymer and peroxide, respectively, and that t and T are the corresponding rates for tritium, then

$$x = cT/tC \qquad (4)$$

The value of x depends upon the concentration of monomer during polymerization, according to the equation

$$1/x = 1 + k_1/k_2[M] \tag{5}$$

from which k_1/k_2 can be found.

EXPERIMENTAL

Monomeric ACN was purified by recrystallization from methanol; the sample of ^{14}C-^{3}H-BPO was obtained by mixing samples of the singly labeled peroxides in solution in chloroform and then precipitating with methanol.

ACN at various concentrations in benzene was polymerized in dilatometers at 60°C in the absence of air to conversions not exceeding 10%. There were no inhibition periods and contraction/time plots were linear. Rates of polymerization are quoted in arbitrary units and are directly proportional to rates in mol/L·s. Polymers were recovered by precipitation in methanol, purified by two precipitations in methanol from benzene solution, and finally dried in vacuum at 40°C.

The initiator and polymers were assayed by liquid scintillation counting in a Packard Tri-carb Model 460C. Samples were individually weighed into standard 20 cm^3 counting vials and dissolved in scintillant (10 cm^3) consisting of Butyl-PBD in AnalaR toluene (0.8% w/v). The polymers gave yellowish solutions and caused appreciable quenching. The UV/visible spectrum of the polymers in toluene did not seriously overlap the fluorescence spectrum of the scintillator so that color quenching was not severe. To ensure satisfactory correction for sample quenching, 10 tritium and 10 carbon-14 standards were prepared using a commercial kit (LKB, catalog no. 1210-124).

Each series was quenched with amounts of inactive polyACN ranging from 0 to 5 g/L. and quench correction curves were prepared using external standardization with the counter in the Automatic Efficiency Control mode. Counting efficiencies ranged from 46 to 29% (^{3}H) with less than 1% overlap into the ^{14}C-region and 74 to 68% (^{14}C) with a maximum of 20% overlap into the ^{3}H-region. All samples were assayed at least three times; good reproducibility was achieved and mean values are quoted. To ensure strict comparability, the initiator was counted in scintillant solution containing various amounts of inactive polyACN. Background measurements also were made using a sample containing inactive polymer.

A test on the removal of unreacted BPO from polymer was performed. Polymer was recovered by the standard procedure from a solution containing polyACN, prepared using unlabeled BPO, mixed with ^{14}C-^{3}H-BPO in proportions similar to those for the actual polym-

TABLE 1. Polymerizations of Acenaphthylene Initiated by ^{14}C-^{3}H-Benzoyl Peroxide

	Experiment no.				
	2	3	4	5[a]	6[b]
[ACN] in mol/L	1.49	2.30	1.16	1.51	-
[^{14}C-^{3}H-BPO] in g/L	3.97	5.41	3.24	3.90	-
Rate of polymerization in arbitrary units	0.85	1.41	0.63	2.62	-
Disintegration rate for polymer:[c]					
^{14}C	70	63	80	31	1
^{3}H	1582	1350	1802	707	23
x calculated from Eq. (4)	0.94	0.99	0.95	0.94	-
k_1/k_2 in mol/L calculated from Eq. (5)	0.09	0.02	0.06	0.09	-

[a] System also contained AIBN at 3.49 g/L.
[b] Test separation, unlabeled polymer and labeled peroxide.
[c] Disintegrations/min/mg; for the peroxide the rates for ^{14}C and ^{3}H were 6,500 and 138,500, respectively.

erizations. The recovered polymer was assayed and found to contain negligible activity (see Table 1), confirming that the procedure for purification of labeled polymers was satisfactory and that the activity associated with them was entirely due to incorporated initiator fragments.

RESULTS AND DISCUSSION

Results are summarized in Table 1. Evaluation of x requires four disintegration rates, and errors lead to considerable scatter in k_1/k_2. The average value of k_1/k_2 for ACN at 60°C is about 0.06 mol/L, which is clearly much smaller than for other monomers such as styrene (0.4), vinyl acetate (1.1), MMA (3.3) [3], vinyl chloride (4.0) [5], and methyl α-cyanoacrylate (17.5) [4]. ACN is therefore found to be very reactive toward the benzoyloxy radical, the value of k_2 being approximately 7 times that for styrene. As pointed out already in connection with the reaction of ACN with the 2-cyano-2-propyl radical [2], it is necessary for some purposes to note that addition of the initiating radical can occur at either of the two equivalent sites in the molecule of ACN but effectively at only one site in the molecule of any of the other monomers.

Using the ^{3}H disintegration rate for the peroxide and that for a derived sample of polyACN, the expression

$$n = 121T/152t \qquad \text{(152 being the molecular weight of ACN)} \qquad (6)$$

allows evaluation of n in Expression (3) for the formula of the average polymer molecule, provided that n is not so small that the initiator fragments contribute appreciably to the weight of the molecule. Unless transfer to initiator is significant, n can be taken as the average kinetic chain length in the polymerization.

From the relationship

$$\text{kinetic chain length} = R_p/R_i \qquad (7)$$

the rate of initiation (R_i) can be found from the overall rate of polymerization (R_p).

The values of n for Polymers 2, 3, and 4 are 70, 82, and 61, respectively; the corresponding values in arbitrary units of $R_i/[BPO]$ are 3.1, 3.2, and 3.2 and are satisfactorily independent of [BPO].

In Experiment 5, polymerization was initiated by a mixture of ^{14}C-^3H-BPO and unlabeled AIBN; the value of n from Eq. (6) is 156 but it does not correspond to a true kinetic chain length since no account is taken of endgroups derived from the azonitrile. If transfer to BPO does not occur, use of this value of n in Eq. (7) leads to a true value for R_i for radicals derived from BPO [6]. For Experiment 5, $R_i/[BPO]$ is 4.3, a value about 1.3 times those for Experiments 2, 3, and 4; the high value could be attributed to the occurrence of more than one process leading to the incorporation of initiator fragments in the polymer. It is necessary to consider initiation, primary radical termination, and the two stages of transfer to initiator. Primary radical termination cannot affect the total rate of incorporation of initiator fragments in polymer, and so it appears that transfer to initiator is appreciable in the system ACN/BPO at 60°C. If the values of $R_i/[BPO]$ for Experiments 2 and 5 are plotted against R_p, the extrapolated value of $R_i/[BPO]$ at $R_p = 0$ is 2.6 and must correspond to the true R_i for both experiments. It can be deduced that approximately 16% of the

BPO fragments in Polymer 2 and 40% of those in Polymer 5 were incorporated as a result of transfer to initiator.

For the present purposes it is necessary to consider whether the balance between benzoate and phenyl endgroups is affected by the occurrence of transfer to initiator; there appears to be no difference between the values of x found for Experiments 2 and 5 but, of course, they are subject to error. The first stage in the transfer process may be represented as

$$P_n\cdot + (C_6H_5.CO.O)_2 \longrightarrow P_n.O.CO.C_6H_5 + C_6H_5.CO.O. \qquad (8)$$

followed by reinitiation either by the benzoyloxy radical or by a phenyl radical derived from it, depending upon the competition between Reactions (1) and (2). Consider the results for Experiment 2 supposing that 84% of the initiator fragments enter polymer by direct initiation, 8% by Reaction (8), and 8% as a result of reinitiation as the second stage of transfer; suppose also that the true value of x applicable to the competing Reactions (1) and (2) is x*. For a total of 100 initiator fragments entering the polymer, the number of benzoate groups is 84x* (from initiation) with 8 (from Reaction 8) and 8x* (from reinitiation) giving an overall value of x as (92x* + 8)/100; the observed value of x is 0.94, indicating that x* is 0.93. Similar calculations for Experiment 5 indicate that x* is 0.92.

The differences between x* and x are too small for reliable detection experimentally. It is not necessary to modify the conclusion that, when the polymerization of ACN at 60°C is initiated by the thermal decomposition of BPO, most of the initiation involves the benzoyloxy radical and that monomeric ACN is about 7 times as reactive as monomeric styrene toward that primary radical.

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