



Acenaphthylene Copolymers. I. Copolymerization Behavior

Jamie Ballesteros , G. J. Howard & Lynne Teasdale

To cite this article: Jamie Ballesteros , G. J. Howard & Lynne Teasdale (1977) Acenaphthylene Copolymers. I. Copolymerization Behavior, Journal of Macromolecular Science: Part A - Chemistry, 11:1, 29-37, DOI: [10.1080/00222337708061249](https://doi.org/10.1080/00222337708061249)

To link to this article: <http://dx.doi.org/10.1080/00222337708061249>



Published online: 05 Dec 2006.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)



Citing articles: 12 View citing articles [↗](#)

Acenaphthylene Copolymers. I. Copolymerization Behavior

JAMIE BALLESTEROS, G. J. HOWARD, and LYNNE TEASDALE

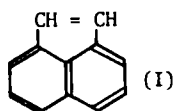
Department of Polymer and Fibre Science
University of Manchester
Institute of Science and Technology
Manchester, England

ABSTRACT

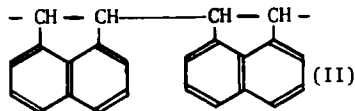
The radical copolymerization of acenaphthylene has been studied with styrene, methyl methacrylate, maleic anhydride, diethyl maleate, and vinylpyrrolidone. Although acenaphthylene is readily polymerizable, unlike most 1,2-disubstituted ethylenes, it has a common feature with this class of monomers in that the Q,e approach is not applicable because of steric effects.

INTRODUCTION

Most 1,2-disubstituted ethylenes exhibit a very low rate of self-addition in polymerization and do not form homopolymers directly although they may often copolymerize quite readily with less sterically hindered monomers. It has been shown by Alfrey and Young [1] that the steric hindrance is most severe in the transition state of the self-addition reaction step. However, acenaphthylene (I) is exceptional in this respect, and it has long been known [2] that this



I



II

1,2-disubstituted ethylene is readily polymerizable. This fact must be attributed to the excessive strain in the five-membered ring, some of which is relieved on formation of the linear polymer (II). As pointed out by Yamada and co-workers [3], the polyacenaphthylene chain might be expected to be inflexible, not only because of the bulky substituent but, in addition, because alternate bonds are locked into the perinaphthylene ring. Consequently a high glass transition temperature is observed, although reported values [4] show marked variation. It should, however, also be recorded that Barrales-Rienda and Pepper [5] find quite normal chain dimensions in solution.

We have prepared several series of copolymers of acenaphthylene with the primary intention of studying the variation of glass transition temperatures with composition. In the present report, however, we take the opportunity to discuss the reactivity of acenaphthylene in radical copolymerizations.

EXPERIMENTAL

The following monomers were employed in the present study. Acenaphthylene (B.D.H.) was twice recrystallized from methanol and stored in the dark; the melting point was recorded as 93°C. Styrene (Fisons) was shaken with caustic soda solution and washed with water to remove inhibitor. After preliminary drying it was fractionally distilled at reduced pressure (40 Torr) and then stored over Molecular Sieves. Methyl methacrylate, diethyl maleate, vinyl-2-pyrrolidone and α -methylstyrene were treated in a similar manner to styrene. Maleic anhydride was twice recrystallized from chloroform to give a product melting at 63°C; trans-stilbene was recrystallized from ethanol and melted at 124°C.

Solvents were dried, redistilled, and stored over a suitable desiccant. Azoisobutyronitrile was recrystallized from toluene, keeping the temperature below 30°C, and was dried in vacuo at room temperature.

Polymerizations were carried out under nitrogen and were stopped by addition of a small quantity of benzoquinone in toluene. Polymers

were precipitated by pouring the reaction mixture into excess methanol. After thorough washing and air-drying, the polymer samples were redissolved, normally in toluene, and reprecipitated as before and washed. The fine powders so obtained were thoroughly dried in vacuo at room temperature.

As the refractive index increment of a copolymer is additive, the weight fraction of the comonomers may be estimated if the increments for the corresponding homopolymers are also measured. Appropriate solvents were selected for each copolymer series to ensure a satisfactory difference between the homopolymer refractive index increments. Four solutions, usually in the concentration range 0.3-1.5% (w/v), were made and were measured at $25 \pm 0.5^\circ \text{C}$ in a PCL differential refractometer. The mean value (ν^*) for the concentration dependence of the optical deviation in the divided cell of the refractometer, which is directly proportional to the true refractive index increment, was used to find the copolymer composition by Eq. (1):

$$\nu_{\text{cop}}^* = w_1 \nu_1^* + (1 - w_1) \nu_2^* \quad (1)$$

where ν_1^* and ν_2^* are the appropriate values for the homopolymers. Elemental analyses were made by the Microanalytical Service, Chemistry Department, UMIST.

We have also attempted to analyze the acenaphthylene-styrene copolymers by nuclear magnetic resonance. Proton magnetic resonance was not successful; the best resolved spectra for poly-acenaphthylene in C_6D_6 exhibited resonance peaks at $4\text{-}5\tau$ attributed to the upfield shift of two aromatic protons by interaction with neighboring aromatic groups; in copolymers, these peaks are of reduced intensity, perhaps as a consequence of a reduced interaction due to the intermediate styrene residues. Preliminary studies with ^{13}C resonance give well resolved spectra which would be suitable for copolymer analysis [8]. Monomer reactivity ratios were found from the copolymer composition equation

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \quad (2)$$

where F_1 is the mole fraction of acenaphthylene in the copolymer and f_1 the mole fraction in the monomer feed. Best values were normally located by the method of intersections and checked by their fit to the raw data.

RESULTS

Copolymerizations with Styrene

Two series of copolymers were prepared, one by radical initiation with azoisobutyronitrile at 60° C in toluene (nine samples) and the second by thermal polymerization in toluene at 110° C (four samples). The mean conversion was 6% and in no instance exceeded 10%. Polymer compositions were determined by measurement of refractive index increments in dioxane solution. Both copolymerizations are adequately described by monomer reactivity ratios of r_1 (acenaphthylene) = 2.3 ± 0.2 and r_2 (styrene) = 0.27 ± 0.02 . Accurate measurements of the initial rates of copolymerization were not attempted. At 60° C, however, the radical homopolymerization of acenaphthylene proceeds at about twice the rate of styrene, and copolymers are formed slightly more slowly than the homopolymers.

Copolymerization with Methyl Methacrylate

A series of nine copolymers was made in toluene solution at 60° C with azoisobutyronitrile as radical initiator to a mean conversion of about 6%. Analysis for copolymer composition was by refractive index increment in toluene solution. The copolymerization results yield r_1 (acenaphthylene) = 1.05 and r_2 (methyl methacrylate) = 0.38.

The polymer conversions show that the homopolymerization of methyl methacrylate is nearly twice that of acenaphthylene. The rate is severely reduced at low mole fractions of acenaphthylene, since the more active radicals (methyl methacrylate) are converted to the less active in a medium consisting largely of the less active monomer, and it remains low over the whole feed composition range (Fig. 1).

A second set of seven copolymers was prepared by thermal polymerization in toluene at 110° C to about 3% conversion. The rate of thermal polymerization of methyl methacrylate and of all the mixed monomers is only about one-tenth of that of acenaphthylene. The copolymer compositions were found both by refractive index increment (in dioxane) and by the carbon content. The data are not in agreement with the results of the radically initiated polymerization at 60° C. A reliable estimate of monomer reactivity ratios could not be obtained, but the values $r_1 = 1.7$ and $r_2 = 1.0$ are in best accord with the experimental data. However, we consider that depropagation of poly(methyl methacrylate) radicals may be of sufficient consequence to prevent the determination of meaningful

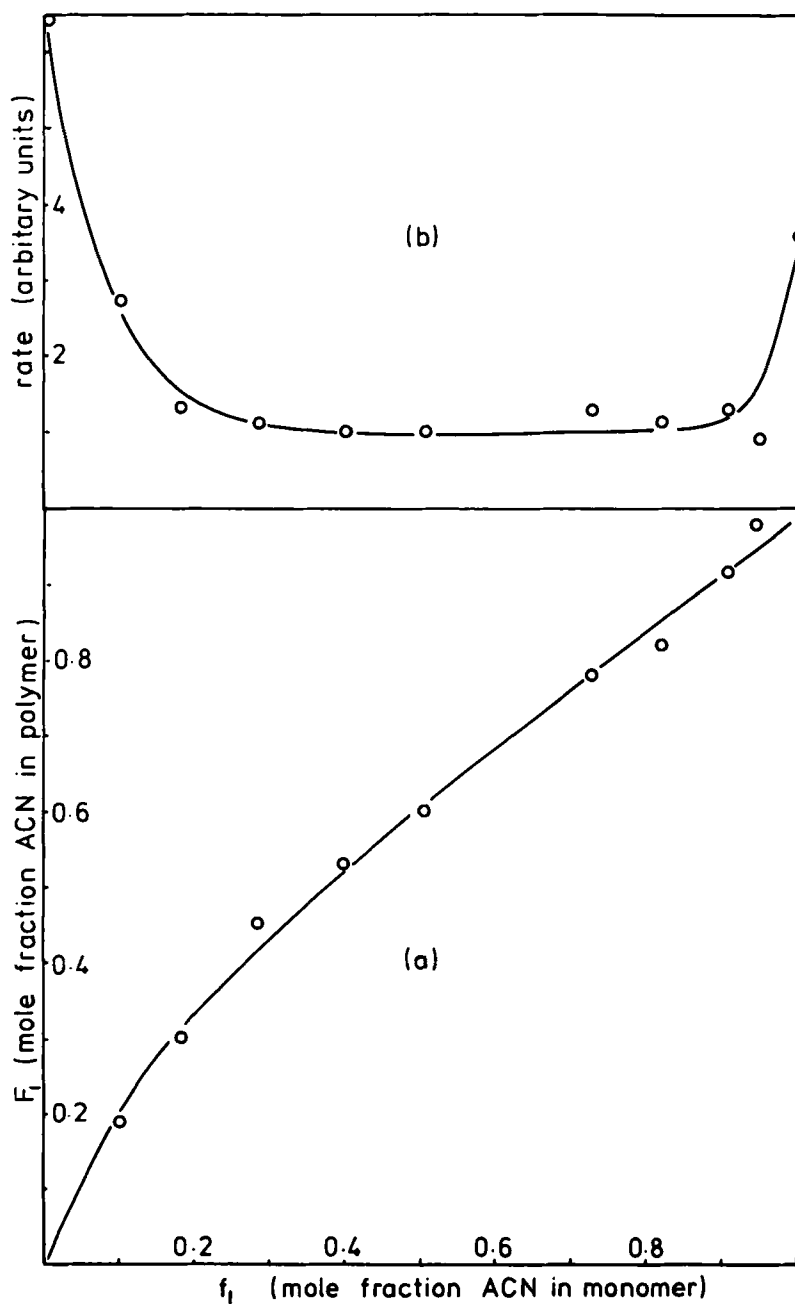


FIG. 1. Plots of (a) composition of acenaphthylene-methyl methacrylate copolymers: (\circ) (60°C , radical initiation) and (—) calcd by Eq. (2) with $r_1 = 1.05$, $r_2 = 0.38$; (b) relative rate of polymerization.

monomer reactivity ratios; such depropagation is not, of course, allowed for in the derivation of the copolymer composition equation.

Copolymerization with Maleic Anhydride

The copolymers (eight samples) were made by radical initiation (azoisobutyronitrile) in dimethylformamide solution at 60°C; the average conversion was 5.4%. The rate of polymerization progressively increases with the acenaphthylene content. Copolymer compositions were found by dissolving weighed samples in benzene and titrating against sodium methoxide solution. The results, shown in Table 1, lead to reactivity ratios of r_1 (acenaphthylene) = 0.50 and r_2 (maleic anhydride) = 0.05, but the copolymers of intermediate composition are not well fitted. Since maleic anhydride does not homopolymerize, it might be expected that r_2 would be zero; many (but by no means all) reported [4] copolymerizations of this monomer lead to monomer reactivity ratios very close to zero. In the present case, the low F_1 values of the first two copolymers listed in Table 1 imply a finite r_2 value. When r_2 is zero, the copolymer composition equation reduces to

$$\frac{(2F_1 - 1)}{(1 - F_1)} = r_1 \frac{f_1}{(1 - f_1)} \quad (3)$$

TABLE 1. Copolymers of Acenaphthylene and Maleic Anhydride

f_1 (mole fraction acenaphthylene in monomer feed)	F_1 (mole fraction acenaphthylene in copolymer)
0.179	0.482
0.279	0.502
0.393	0.628
0.489	0.641
0.658	0.677
0.719	0.701
0.816	0.747
0.901	0.815

but the present data are not in accord with this equation. That is, if $r_2 = 0$, penultimate group effects in radical reactivity would have to operate and we estimate values of $r_1' = 2.2$, $r_1 = 0.2$. Of course, any treatment placing $r_2 = 0$ necessarily disregards the low f_1 data of Table 1.

Copolymerization with Diethyl Maleate

Seven copolymers were made by radical initiation at 60° C in various toluene-dimethylformamide mixtures; the average conversion was 7%. Analysis for copolymers by refractive index increment is not feasible in the absence of a value for poly(diethyl maleate). The carbon content was employed to determine copolymer compositions. The method of intersections shows that r_2 is very small and actually appears to be slightly negative. We have, therefore, assumed r_2 to be zero and applied Eq. (3), which is satisfied by a value of r_1 (acenaphthylene) of 4.7.

Copolymerization with N-Vinylpyrrolidone

A series of seven copolymers was prepared by radical initiation at 60° C in toluene-dimethylformamide mixtures. Conversions were about 8%, and it was found that the approximate rate of polymerization increased steadily with the acenaphthylene content. The copolymer composition was found by measurement of the refractive index increment in dioxane solution; nitrogen contents although low are quite consistent with the refractive index data. The compositional data, given in Table 2, do not lead to a satisfactory selection of monomer reactivity ratios. Clearly r_2 is very low but cannot be zero since vinylpyrrolidone is readily homopolymerized; considerable penultimate group effects are indicated by our results.

Other Copolymerizations

A limited number of copolymerizations were made with α -methylstyrene and with trans-stilbene, but no reactivity ratios were obtained. In the former case, excessive depropagation of α -methylstyrene at 60° C made the effective mole fraction of monomer uncertain. No satisfactory method for finding the composition of the stilbene copolymers could be found although their refractive index increments confirmed that a progressive series of copolymers had been formed.

TABLE 2. Copolymers of Acenaphthylene and N-Vinylpyrrolidone

f_1 (mole fraction acenaphthylene in monomer feed)	F_1 (mole fraction acenaphthylene in copolymer)
0.127	0.771
0.195	0.823
0.267	0.862
0.328	0.872
0.422	0.887
0.685	0.912
0.785	0.937

DISCUSSION

The ring strain in acenaphthylene confers a ready polymerizability on this monomer, and in all the copolymerizations studied here it is preferentially combined into the copolymer. It must, however, not be assumed that the steric effects common to 1,2-disubstituted ethylenes are entirely absent in chain radical propagation reactions. It is well known that the Q, e scheme is unable to accommodate steric influences in copolymerization [1] and that Q, e values for 1,2-disubstituted ethylenes have little meaning. Our data for the copolymerization (radical 60°C) of acenaphthylene with styrene gives $Q = 2.13$ and $e = -0.11$, whereas the radical copolymerization with methyl methacrylate leads to $Q = 2.87$ and $e = 1.36$! The monomer reactivity ratios in the former copolymerization (thermal, 90°C) are reported by Ueberreiter and Krull [6] as $r_1 = 3.81$, $r_2 = 0.33$; since $r_1 r_2 > 1$, it is not possible to calculate a real value for e_1 . It should be noted that the entry in the Polymer Handbook [4] has transposed the reactivity ratios for these monomers. The radical-initiated copolymerization of acenaphthylene with methyl methacrylate has also been reported [7], and monomer reactivity ratios of $r_1 = 2.25$, $r_2 = 0.44$ are given, from which $Q = 1.75$, $e = 0.50$. Other estimates of the Q, e values for acenaphthylene may be made from the limited number of other copolymerization reported [4], although these involve less well established Q, e values for the second monomer. No consistency whatsoever may be found in these Q, e estimates for acenaphthylene, and we

conclude that the steric interferences in copolymerization of this hindered monomer are sufficient to make the Q,e approach inapplicable.

ACKNOWLEDGEMENTS

One of us (L.T.) is indebted to the Science Research Council for the award of an Advanced Course Studentship. We are grateful to Dr. F. Heatley, Chemistry Department, University of Manchester for his recording and interpretation of nuclear magnetic resonance spectra.

REFERENCES

- [1] J. Alfrey and L. J. Young, in Copolymerization, G. E. Ham, Ed., Interscience, New York, 1964.
- [2] K. Dziewanski and Z. Lylso, Ber., 47 1679 (1914).
- [3] A. Yamada, M. Yanagita, and E. Kobayashi, J. Polym. Sci., 61, 514 (1962).
- [4] J. Brandrup and E. H. Immergut, Eds., Polymer Handbook 2nd ed., Wiley-Interscience, New York, 1975.
- [5] J. M. Barrales-Rienda and D. C. Pepper, Polymer, 8, 351 (1967).
- [6] K. Ueberreiter and W. Krull, Z. Physik. Chem., 12, 303 (1957).
- [7] K. Noma, M. Nima, and H. Norisada, Doshisha Daigaku Rikogaku Kenkyu Hokoku, 10, 349 (1970); Chem. Abstr., 73, 77680m (1970).
- [8] F. Heatley, private communication.

Accepted by editor April 8, 1976

Received for publication May 5, 1976