Acenaphthylene Copolymers. I. Copolymerization Behavior

Jamie Ballesteros[a]; G. J. Howard[a]; Lynne Teasdale[a]
[a] Department of Polymer and Fibre Science, University of Manchester Institute of Science and Technology, Manchester, England

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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 steri-
cally 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 excep-
tional in this respect, and it has long been known [2] that this
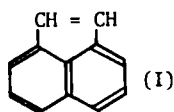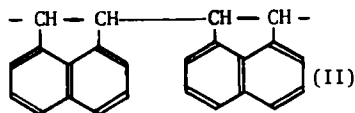
I   II

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 tem-
perature 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 transi-
tion 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 chloro-
form to give a product melting at 63° C; trans-stilbene was recrystal-
lized 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 meth-
anol. 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 incre-
ments 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 $25 \pm 0.5°C$ in a
PCL differential refractometer. The mean value $(\nu*)$ for the con-
centration dependence of the optical deviation in the divided cell of
the refractometer, which is directly proportional to the true refrac-
tive index increment, was used to find the copolymer composition
by Eq. (1):

$$\nu*_{cop} = w_1\nu_1* + (1 - w_1)\nu_2* \tag{1}$$

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 $4-5\tau$ 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

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

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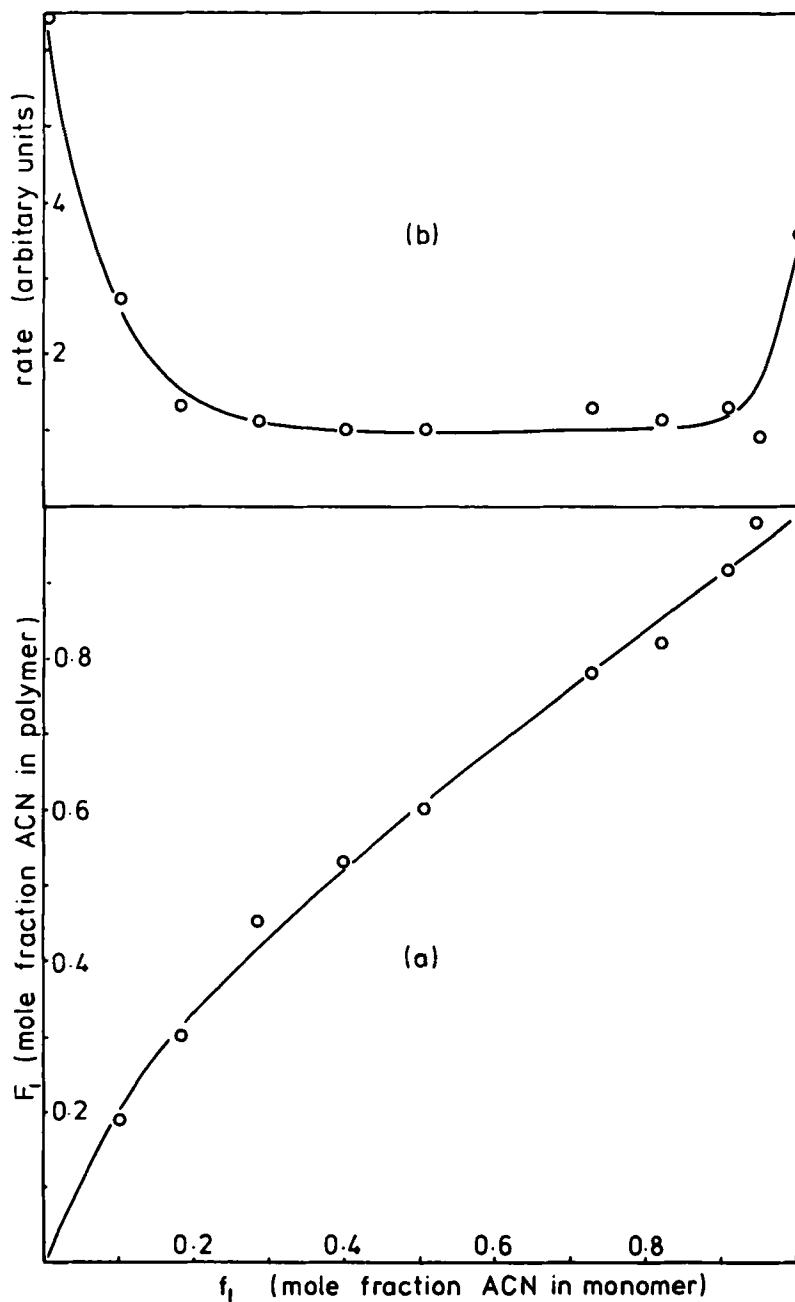
FIG. 1. Plots of (a) composition of acenaphthylene–methyl meth-
acrylate copolymers: (o) (60° C, radical initiation) and (—) calcd
by Eq. (2) with r_1 = 1.05, r_2 = 0.38; (b) relative rate of polymerization.

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 progres-
sively increases with the acenaphthylene content. Copolymer com-
positions 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

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

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 $r_1r_2 > 1$, 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

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