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Acrylonitrile Copolymerizations. III. Flash Pyrolysis of Methyl Methacrylate and Styrene Copolymers

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SUMMARY

Flash pyrolysis of the copolymers acrylonitrile-methyl methacrylate and acrylonitrile-styrene has been carried out over the whole range of compositions, and yields of the monomers have been measured. In the first case, all of the methyl methacrylate is recovered as monomer except when a unit is isolated between two acrylonitrile segments. However, the yield in acrylonitrile monomer is lower; it corresponds to the units isolated between long sequences of methyl methacrylate plus the isolated acrylonitrile diads. The agreement between the calculated and experimental yields is excellent only if one takes into account the penultimate effects. In the second case, however, it is not possible to deduce a quantitative interpretation of the yields of either styrene or acrylonitrile monomers.

INTRODUCTION

In two preceding papers [1, 2], we have shown the occurrence of penultimate and antepenultimate effects on the reactivity of chain-end radicals in acrylonitrile (A) copolymerizations with styrene (S) or methyl methacrylate (M). In the latter case, the consequences of these effects on the distribution of the M sequences have been investigated using IR and NMR spectroscopy. However, the direct application of these methods is limited to favorable cases. We have therefore tried to use a new method that might prove more generally applicable: flash pyrolysis. Recently, this technique was successfully applied to the study of the sequences in ethylene-propylene copolymers [3]. It is well known that S and M homopolymers give high yields of monomers while polyacrylonitrile gives a few volatiles and a very limited yield of monomer. Our purpose is to determine if the yields in different monomers may be dependent on the sequence distribution and to describe such dependence quantitatively.

Flash pyrolysis has already been applied to AS copolymers, and in 1965 Lebel [4] showed that it is possible to distinguish between a true copolymer and a mixture of homopolymers. More recently, Shibazaki [5] deduced from pyrolysis results, a parameter, β_A, of the boundary effect of the sequences defined as the ratio of the probabilities P_{AB} and P_{AA} that A-type monomer units will result from the decomposition of macroradicals ended, respectively, by two different units, A and B, and by two A units. Shabazaki stated that β is dependent on temperature but not on sequence distribution.

There are no published results on flash pyrolysis of AM copolymers. However, Grassie and Farish [6] have shown that slow pyrolysis of these copolymers is initiated in the M sequences and is propagated by depolymerization of the resulting radicals.

EXPERIMENTAL

The preparation of copolymers in the whole range of compositions has been described previously [1].

Flash pyrolysis was carried out using a Fisher Pyromatik apparatus with a platinum filament heated by Joule effect, the temperature being measured with a thermocouple fixed to the filament. The copolymer was deposited on the filament from 3 µl of a 0.2% solution. The solvent, vaporized before pyrolysis, was $CHCl_3$ for the copolymer containing less than 50% molar of A, and $CHCl_3$-$HCON(CH_3)_2$ mixtures for the others. The solution also contained 0.01% of poly-α-methylstyrene. This polymer gives a 100% yield of monomer on flash pyrolysis and was used as internal concentration standard. This point, and the fact that its presence does not change the yields of A, M, or S in the pyrolysis conditions used, have been verified because it has been shown that at lower temperatures (less than 300°C) poly-α-methylstyrene may induce the degradation of some polymers such as polystyrene (PS) or polyvinylchloride [7, 8].

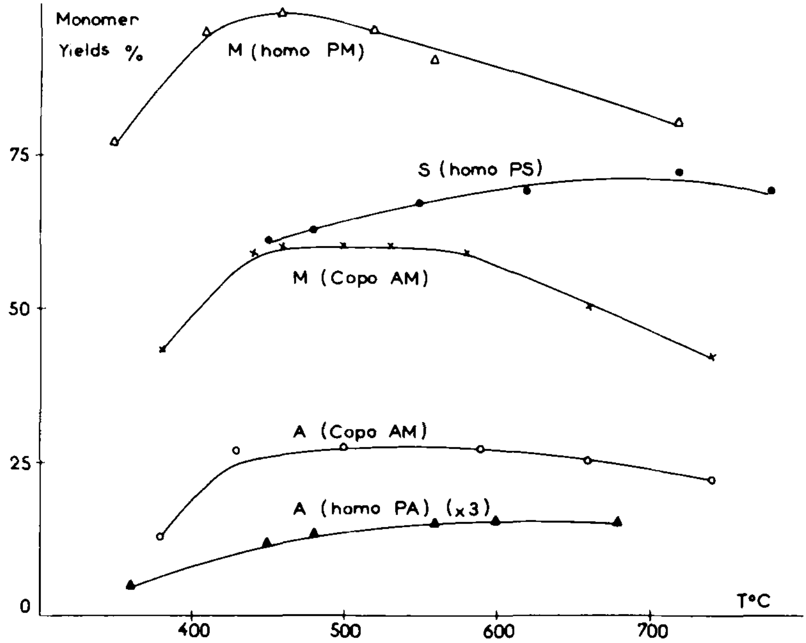

Fig. 1. Yields (molar per cent) of M, A, and S as a function of the pyrolysis temperature for the three homopolymers and a copolymer M (52.5%)-A (47.5%).

The yields of monomers increased with the duration of pyrolysis and leveled off after about 10 sec. In this study, pyrolysis was stopped after 12 sec. Yields are also largely dependent on the temperature, as shown in Fig. 1. From these results we adopted the following conditions: 460°C for AM copolymers and 560°C for AS copolymers. Under these conditions, there was practically no formation of products lighter than the monomers.

The pyrolysis chamber, with glass walls, was directly coupled with the injector of a Varian-Aerograph 1200 GLC apparatus. The column (2 m long, 2 mm internal diam) was filled with Chromosorb W impregnated with 5% of Ucon Polar 50 HB 2000 and was operated at 100°C. Detection was carried out by flame ionization. The carrier gas was nitrogen.

Some products heavier than the monomers may be formed. They are generally deposited on the wall of the pyrolysis chamber. In some experiments efforts were made to detect them after warming this wall at 100-120°C. Then a column was filled with a thermostable polymer prepared in the laboratory and was operated between 200 and 300°C.

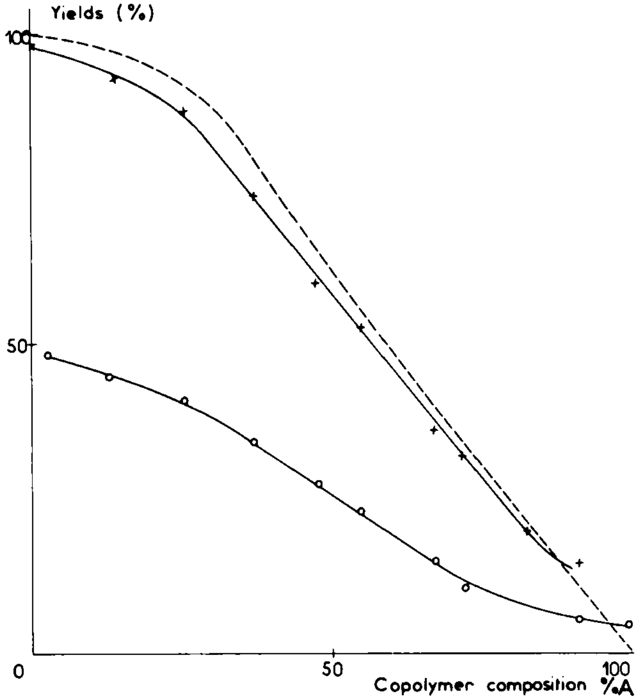

Fig. 2. Yields (molar per cent) of M (X) and A (o) monomers as a function of the molar copolymer composition. The dotted line is calculated for the molar per cent of M sequences longer than one M unit.

Some parallel experiments were also carried out. Thermogravimetric analyses (TGA) were done using a Ugine-Eyraud B 60 thermobalance in programmed heating at 3 or 11°C/min up to 600°C. Finally, some mass spectrometric analyses were carried out in an Atlas CH4 apparatus capable of rapid scanning. The polymer was deposited as a film in the crucible of the solids introduction and heated up to 500°C in 3-4 min. Spectra were taken at different temperatures, using a low ionization voltage (9 eV).

RESULTS AND DISCUSSION

Acrylonitrile-Methyl Methacrylate Copolymers

TGA experiments show that the copolymers rich in M units (M > 75%) leave no solid residue after heating to 600°C. For moderate degradation (weight loss < 10%), GLC analysis of trapped volatile products indicates the presence of M monomer only. Acrylonitrile appears later at about 10-15% degradation. The products remain soluble up to more than 20% degradation. For the copolymers less rich in M units a solid residue is observed. Its amount increases with the A content of the copolymer up to 50% for PA homopolymer. It depends also on the heating rate, and for a copolymer with 79 molar % of A the residue levels off at 45% at 400°C for a heating rate of 3°C/min, but for a heating rate of 11°C/min, the weight loss increases smoothly up to 64% at 970°C. Correspondingly, in the flash pyrolyses which correspond to very much higher heating rates, the residue seems to be less important.

In the experimental conditions adopted, the volatile products from flash pyrolysis are essentially the monomers. Heavier products may be recovered in noticeable amounts only if the A content is greater than 75%, and their amount increases with the A contents. The yields in monomers are shown in Fig. 2 as a function of A content. When the A content increases, both the yields of M and A decrease; as expected, the behavior of the two different units is reverse—the yield of M decreases continuously from 95% to near 0 with the M content, while the yield of A decreases from 50% only to about 5% when the A content increases.

In attempting to confirm the occurrence of penultimate effects, it seemed to be interesting to interpret these results in terms of the boundary parameter, β, of Shibazaki, because β is a function of the run number R defined by Harwood [9] as the number of A or B sequences in 100 monomeric units of a copolymer AB as

$$\beta_A = 1 - \left[\Phi_A - \frac{Y(A)}{Y_0(A)}\right]\frac{200}{R}$$

where Φ_A is the molar fraction of A monomer units in the copolymer, Y(A) the yield of A monomer obtained in the pyrolysis of the copolymer, and $Y_0(A)$ the corresponding yield for the A homopolymer. R is related to the reactivity ratios r_A and r_B by the relation

$$\frac{200}{R} = 2 + r_A x_A + r_B x_B$$

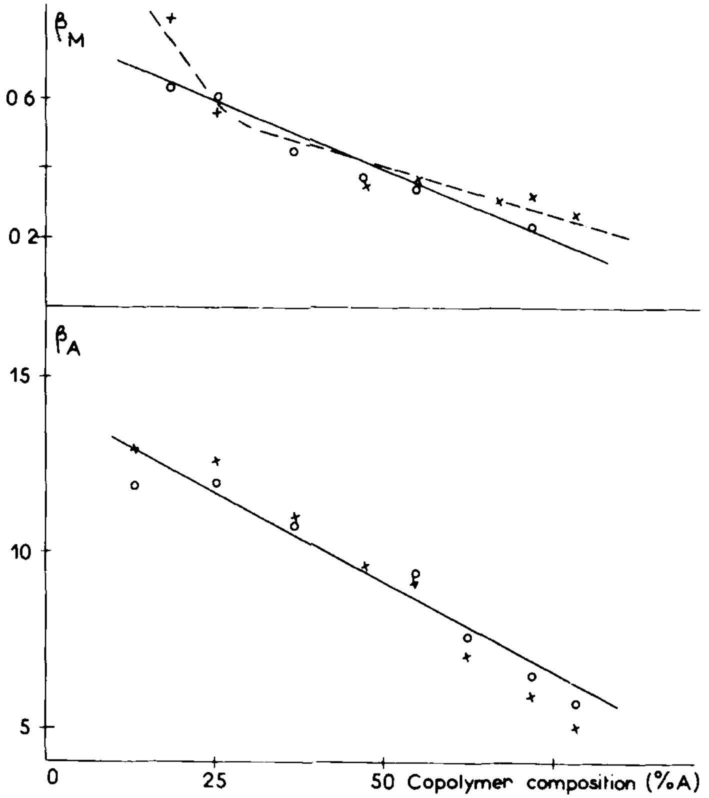

Fig. 3. Shibazaki boundary parameters β_A and β_M as a function of the molar copolymer composition; calculation takes into account (○) or does not take into account (+) the penultimate effects.

where $x_A = A/B = 1/x_B$ is the molar ratio of A and B monomer concentrations in the monomer feed used for the copolymerization. If one takes into account the penultimate effects, one gets

$$\frac{200}{R'} = 2 + \frac{1 + r_{BB}/x_B}{1 + x_A/r_{AB}} + \frac{1 + r_{AA}x_A}{1 + x_B/r_{BA}}$$

The values so calculated for β_A and β_M are plotted in Fig. 3 against the molar A content in the copolymer. We have used the values determined previously [1]: $r_A = 0.25$ and $r_M = 1.17$ when the penultimate effects are not considered, and, when they are considered, $R_{AA} = 0.39$,

$r_{MA} = 0.22$, $r_{AM} = 1.56$, and $r_{MM} = 1.02$. The statement of Shibazaki that the values of β are not dependent on the copolymer composition is not verified, since both β_A and β_M decrease with the M content. However, the discrepancy between the extreme values is a little less important if one considers the penultimate effects. The theory of Shibazaki considers only the propagation of the degradation reaction and neglects the initiation reaction, implicitly admitting that it would be at random. In the present case the initiation takes place chiefly in the M sequences, so that the β parameter may be without significance.

The low yield of M for copolymers rich in A suggests that the isolated M units may not be recovered. In Fig. 2 the dotted curve gives the fraction of M units which belong to sequences greater than one. In the whole composition range the experimental curve is very close to it, so that it seems to be the rule that only the isolated M (M_1 sequences) are not recovered. Unfortunately, as stated previously [2], the fraction of the M_1 sequences is not much changed, whether or not one takes into account the penultimate effects. However, the present results show that the breaks are not initiated in the AM sequences but only in the MM sequences.

The data obtained from pyrolysis in the mass spectrometer confirm that some of the M units are not recovered as monomer, because mass 153, corresponding to a codimer AM, is obtained in a yield increasing with the A content, together with heavier products (among them, it seems, oligomers of acrylonitrile). These results suggest that the A units adjacent to isolated M units cannot be recovered as monomer.

The rather high yield in A for the copolymers rich in M suggest that the isolated A units, other than those adjacent to isolated M units, are all recovered in 100% yield. However, when the A content increases, the amount of such isolated units becomes lower than the experimental yield so that other sequences give A monomer. The low yield of A (5%) for the PA homopolymer shows that the long sequences may give some A, and we have assumed that this yield remains unchanged in the copolymers for the long sequences of A($\geqslant$ 10 units). We have assumed also that the A diads (A_2 sequences) give A monomer in pyrolysis. One might suppose, from the value of β_A of Shibazaki, that these diads would give dimer. Indeed, one of the heavier products of the pyrolysis has been identified by GLC retention time as the dimer α-methylene-glutaronitrile, but the yield of this product is the highest for PA homopolymer; it decreases rapidly when M content increases and is practically negligible when the A content is less than 70%. This result is confirmed by mass spectrometry analysis which shows that the yields of heavy products, among them mass 106, decrease

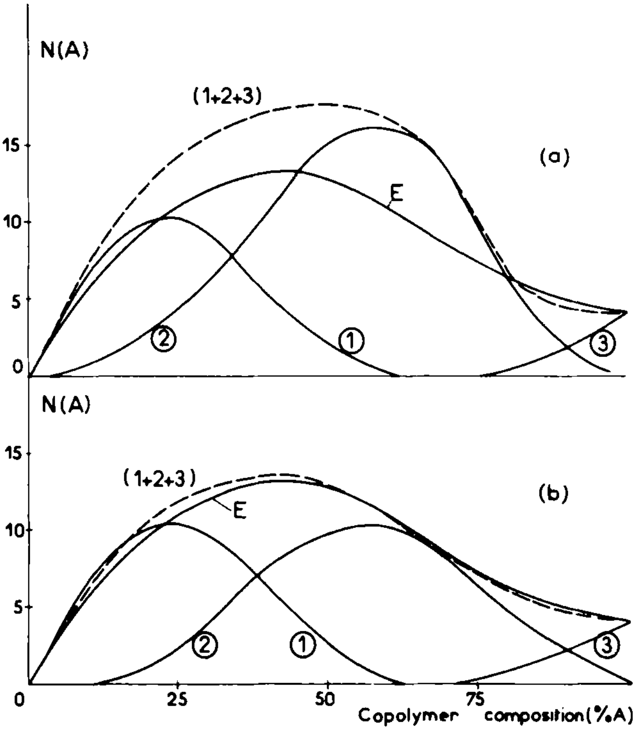

Fig. 4. Molar per cent numbers of A in MMAMM pentads (curves 1), in diads A_2 (curves 2), and 5% of A in A > 10 sequences (curves 3), cumulatives curves (1 + 2 + 3), and experimental molar per cent numbers of recovered A (E). (a) Without penultimate effects, (b) penultimate effects taken into account.

rapidly with the A content of the copolymers. On the other hand, as shown in Fig. 4, the weight fraction of the A unit belonging to A_2 sequences is maximum for an A content of 55%. In the same figure are plotted [taking in account (b) or not (a), the penultimate effects], the fraction of A belonging to A_1 sequences isolated between two long M sequences (or the fraction of pentads MMAMM) (curves 1(a) and 1(b)), the fraction of A_2 sequences (curves 2(a) and 2(b)), and 5% of the fraction of A > 10 sequences which represents the contribution of long sequences (curves 3(a) and 3(b)), and the cumulative curves (1 + 2 + 3), together with the experimental curve. The calculations used to build curves 1, 2, and 3 are given in the Appendix. Figure 4(b) shows a striking agreement between the cumulative curve and the experimental one, and in our opin-

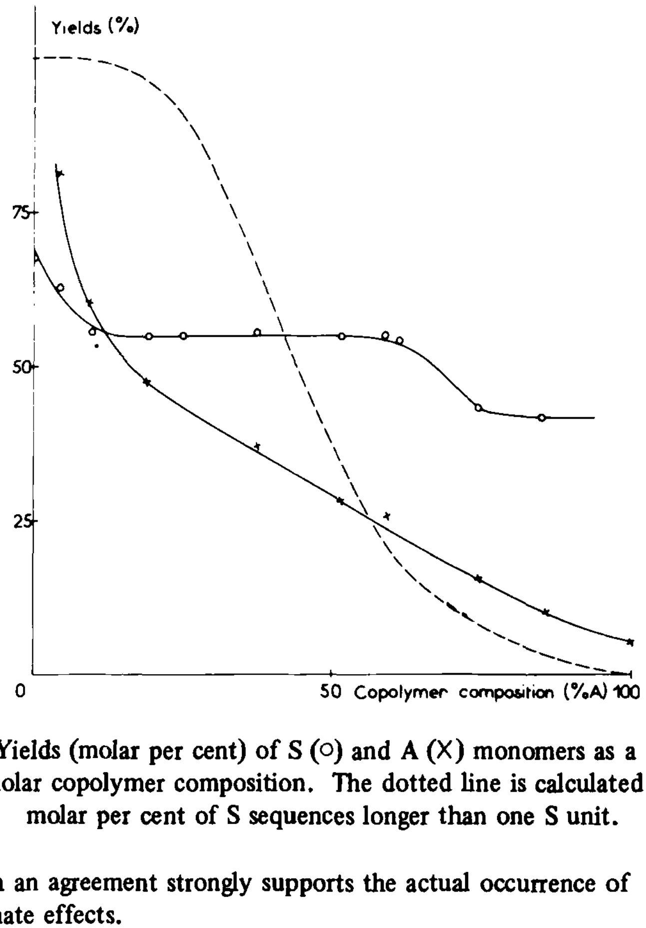

Fig. 5. Yields (molar per cent) of S (o) and A (X) monomers as a function of the molar copolymer composition. The dotted line is calculated for the molar per cent of S sequences longer than one S unit.

ion, such an agreement strongly supports the actual occurrence of penultimate effects.

Thus, for the couple A-M, flash pyrolysis is shown to give accurate data about the actual sequence distribution, especially for the M_1, A_1, and A_2 sequences.

Acrylonitrile-Styrene Copolymers

The behavior of the AS copolymers is different, as shown in Fig. 5 where the yields in A and S monomers are plotted against the molar per cent of A. The yield of styrene is initially rather low, 67%. Benzene and toluene are well detected, but account for only a very limited amount of styrene units, so that the other products are heavier products; several of them have been detected in the pyrolysis GLC diagram of polystyrene.

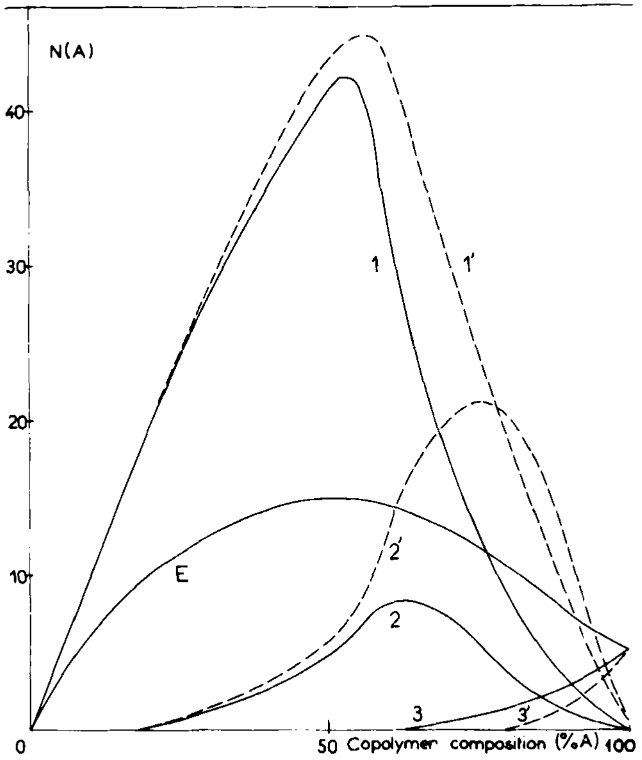

Fig. 6. Calculated molar per cent number of A in A_1 (curves 1), A_2 (curves 2) sequences in the AS copolymer, and 5% of A in A $\geqslant$ 10 sequences (curves 3), and experimental molar per cent number of A recovered (E). For the dotted curves (1', 2', 3') the calculations do not take into account the penultimate effect.

They have not been identified in the present work, but the reader is referred to a recent paper by Noffz et al. [10]. In the copolymers, the yield in these products smoothly decreases, while the yield in S takes a limit value of 55%. Probably the yield in S is higher for the shortest S sequences. The dotted line, calculated for the S units belonging to sequences longer than one unit, crosses the S yield curve, showing that, contrary to the case of the AM copolymers, a high per cent of isolated S units gives monomer. Thus, in this case the probabilities of breaking S–S and S–A bonds are close together. This is confirmed by the rather high yield of A monomer for the low-A-content copolymers. The

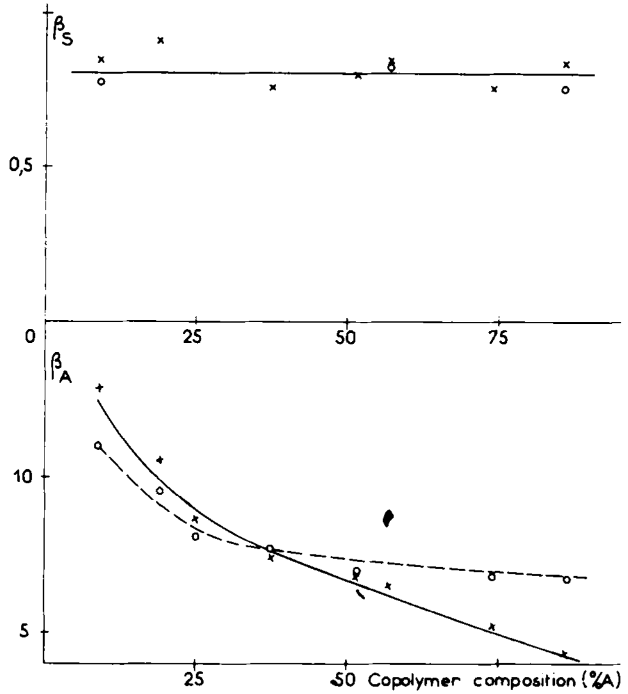

Fig. 7. Shibazaki boundary parameters β_A and β_S as a function of the molar copolymer composition. Calculation takes into account (o) or does not take into account (+) the penultimate effects.

yield in A decreases smoothly as the A content increases, but again the exact behavior is very different from that of the MA copolymers. Figure 6 shows the calculated curves for the A_1 and A_2 sequences, taking and not taking into account the penultimate effects. It is obvious that the experimental curve cannot be related to any of the calculated curves or combinations of them. Thus, neither S nor A monomer yields is related simply to the sequence distribution. On the other hand, as shown by the curves in Fig. 7, the boundary parameters β_S and even β_A, if one takes into account the penultimate effects (with $r_{AA} = 0.33$, $r_{SA} = 0.08$, $r_{SS} = 0.30$, and $r_{AS} = 0.55$ in lieu of $r_A = 0.07$ and $r_S = 0.39$), are not very dependent on the copolymer composition, obeying rather well Shibazaki's statement. Possibly this means that the probability of breaking a S—A or an A—S bond is not dependent upon the nature of the remote units. Then the yield in S monomer from isolated units may be noticeable and only a little bit lower than that from longer sequences. However, one would expect that, if for a copolymer with a high degree of alternation, as for a 50-50 copolymer in the present case, the yield in one monomer had a high value, the yield for the other would be about the same. Actually, the yield of A, which is rather high when the A units are isolated in long S sequences (low A content), is about half that of the S yield for an alternate copolymer. In our opinion, this is due to the fact that the pyrolysis experiments were carried out with a bulk sample where the polymer chains were not separate. Then we have to consider the possibility of intermolecular reactions and also intermolecular association; this is particularly true for the A unit which may undergo dipole couplings via the nitrile groups [11]. We have already shown [1] that such couplings cause kinetic effects during the copolymerization of A with M or S monomers.

Then another question arises: Why are these effects not operative in the case of A-M copolymers, or, at least, why do they allow unperturbed pyrolysis behavior of A_1, A_2, and M_1 sequences?

CONCLUSION

The data reported here show that in the favorable case of A-M copolymers, flash pyrolysis permits the elucidation of some details of sequence distribution, and notably, the data support the occurrence of penultimate effects during the synthesis of the copolymer. This is possible, first, because there is a great difference in the depropagation rates for isolated monomer units or units in diads and those in longer sequences, and second, because in short sequences intermolecular dipole couplings are not important. These two conditions are not expected to be valid for a number of copolymers. However, a complete study of the volatile pyrolysis products other than the monomers would possibly give, in a number of cases, useful information concerning the sequence distribution in the copolymers. Such a study would require the total recovery of volatiles, their separation, identification, and quantitative analysis. Recently Cantow and his associates reported their results on ethylene copolymer [12]. Similar work is being carried out in our laboratory on A-S and A-M copolymers.

APPENDIX

Relationships are taken from Miller and Nielsen [13]. If A and B are the molar fractions of monomers and x = A/B is their molar ratio, the probabilities that a given chain end will add a given monomer are:

for terminal model:

that a chain ending in $A^{\bullet}$ will add an A monomer: $P_{AA} = \dfrac{r_A x}{1 + r_A x}$

" " " $A^{\bullet}$ " " B " $P_{AB} = \dfrac{1}{1 + r_A x}$

" " " $B^{\bullet}$ " " B " $P_{BB} = \dfrac{r_B}{x + r_B}$

" " " $B^{\bullet}$ " " A " $P_{BA} = \dfrac{x}{x + r_B}$

for penultimate model:

that a chain ending in $AA^{\bullet}$ will add an A monomer: $P_{AAA} = \dfrac{r_{AA} x}{1 + r_{AA} x}$

" " " $AA^{\bullet}$ " " B " $P_{AAB} = \dfrac{1}{1 + r_{AA} x}$

" " " $BA^{\bullet}$ " " A " $P_{BAA} = \dfrac{r_{BA} x}{1 + r_{BA} x}$

" " " $BA^{\bullet}$ " " B " $P_{BAB} = \dfrac{1}{1 + r_{BA} x}$

" " " $BB^{\bullet}$ " " B " $P_{BBB} = \dfrac{r_{BB}}{x + r_{BB}}$

" " " $BB^{\bullet}$ " " A " $P_{BBA} = \dfrac{x}{x + r_{BB}}$

that a chain ending in $AB^{\bullet}$ will add an B monomer $P_{ABB} = \frac{r_{AB}}{x + r_{AB}}$

" " " $AB^{\bullet}$ " " A " $P_{ABA} = \frac{x}{x + r_{AB}}$

The following calculations are for the methyl methacrylate-acrylonitrile system, but similar relationships may be calculated for the styrene-acrylonitrile system.

Molar fraction of isolated M units

terminal model: $\omega_M\,[1] = P^2_{MA}$

penultimate model: $\omega'_M\,[1] = \frac{P_{MMA}P_{AMA}}{P_{MMA} + P_{AMM}}$

Molar fraction of isolated A units

terminal model: $\omega_A\,[1] = P^2_{AM}$

penultimate model: $\omega'_A\,[1] = \frac{P_{AAM}P_{MAM}}{P_{AAM} + P_{MAA}}$

Molar fraction of diads A_2

terminal model: $\omega_A\,[2] = 2P^2_{AM}P_{AA}$

penultimate model: $\omega'_A\,[2] = \frac{2P^2{}_{AAM}P_{MAA}}{P_{AAM} + P_{MAA}}$

Fraction of A units centered in the pentad $MM\overset{*}{A}MM$

penultimate model

$$f_{[MM\overset{*}{A}MM]} = f_{[M\overset{*}{A}M]}P^2_{AMM}$$

or

$$f_{[M\overset{*}{A}M]} = f_{[AB]}P_{MAM}/A$$

and

$$f_{[AB]} = \frac{1}{2 + \frac{P_{AMM}}{P_{MMA}} + \frac{P_{MAA}}{P_{AAM}}}$$

Then

$$f_{[MM\overset{*}{A}MM]} = \frac{1}{A}\left[\frac{1}{2 + \frac{P_{AMM}}{P_{MMA}} + \frac{P_{MAA}}{P_{AAM}}}\right]P^2_{AMM}P_{MAM}$$

terminal model: calculations are carried out, setting

$$r_{AA} = r_{MA} = r_A \quad \text{and} \quad r_{MM} = r_{AM} = r_M$$

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