

## Pyrolysis of Random and Block Copolymers of Ethyl Acrylate and Methyl Methacrylate

KARL L. WALLISCH, *Rohm and Haas Company,  
Philadelphia, Pennsylvania 19137*

### Synopsis

Pyrolysis gas chromatography can distinguish random from block copolymers of ethyl acrylate and methyl methacrylate. The pyrograms depend on the pyrolytic temperature, the ratio of copolymerized monomers, the degree of conversion, and the method of polymerization. Larger amounts of ethyl methacrylate and methyl acrylate are formed on pyrolysis of random copolymers than of block copolymers. The presence of mixed dimers indicates random copolymerization. The sum of the percent recovery of ethyl alcohol and ethyl acrylate is fairly constant over a range of compositions and monomer sequence. Random copolymers produce less ethyl alcohol than ethyl acrylate on pyrolysis, while homopolymers and block copolymers produce more ethyl alcohol and less ethyl acrylate. In a set of random copolymers with different EA/MMA ratios, there is an increasing per cent recovery of EA monomer with decreasing EA in the copolymer, while ethyl alcohol shows the opposite behavior. The characteristic degradation patterns are thought to be governed by the availability of the tertiary hydrogen for abstraction by the alkoxy oxygen of a neighboring acrylate unit, the availability depending on the sequence distribution of acrylate/methacrylate molecules.

### INTRODUCTION

Pyrolysis gas chromatography of acrylic and methacrylic polymers has been reported by many investigators. Radell<sup>1</sup> reports methyl methacrylate (MMA) in the pyrolyzate of polymethyl acrylate and ethyl methacrylate in the pyrolyzate of ethyl acrylate (EA) homopolymer. Barrall et al.<sup>2</sup> and Bombaugh et al.<sup>3</sup> point out some differences in the alcohol production of random copolymers and mixed polymers of acrylates and ethylene. They suggest that neighboring rather than isolated ester groups are mechanistically involved in the alcohol formation. They also report<sup>3</sup> that a random copolymer of methyl acrylate and ethylene produces less methanol on pyrolysis than the corresponding block copolymer. Grassie et al.<sup>4</sup> report the absence of methanol in low-conversion (approximately 5%) methyl methacrylate/methyl acrylate (2/1) copolymer.

McCormick<sup>5</sup> observed increasing amounts of pyrolytic ethyl acrylate when the ethyl acrylate content of an EA/MMA copolymer was decreasing. Noffz<sup>6</sup> reports the dimers and mixed dimers of ethyl acrylate and selected acrylates in homo- and copolymers. Daniel et al.<sup>7</sup> show that the amount of alcohol (butanol and 2-ethylhexanol) formed in the course of pyrolysis

depends upon whether acrylic or maleic acid ester is copolymerized. In a study of methyl acrylate homopolymer, Cameron<sup>8</sup> suggests that the precursor for the formation of methanol and CO<sub>2</sub> is a common free radical which could be formed after the transfer of an  $\alpha$ -hydrogen atom. Ferlauto et al.<sup>9</sup> investigated the relationship of ethyl acrylate yield and the number of ethyl acrylate-methyl methacrylate bonds contained in the copolymer. Gatrell and Mao<sup>10</sup> observe larger methyl acrylate (MA) monomer recovery from the copolymer of a 1:1 MA/MMA than from a 1:1 mixture of the homopolymers. Dandoy and Dencubourg<sup>11</sup> report ratio differences of EA/EtOH peak heights between low- and high-conversion copolymers of EA/MMA, but do not elaborate.

The main objective of this investigation was to further evaluate pyrolytic gas chromatography as an analytical tool to differentiate among the homopolymers and the random and block copolymers of ethyl acrylate and methyl methacrylate.

## EXPERIMENTAL

### Preparation of Reference Polymers

Detailed procedures for the polymer preparations have been described.<sup>12</sup>

*Homopolymers* were prepared by a single-stage reflux polymerization process.<sup>12</sup> Commercially available monomers were used throughout the experiments. Neither the inhibitor was removed from the monomer, nor were other purifications made.

*Random copolymers* were prepared also by a single-stage reflux polymerization process.<sup>12</sup> The monomers were mixed prior to being added to the emulsion. The conversion was high, with less than 0.1% residual monomer left. In this fashion, a highly random copolymer can be prepared with short blocks of EA and MMA alternating in spite of the fact that a certain degree of compositional drift may not be avoided.

*Block copolymers* were prepared also by reflux polymerization process.<sup>12</sup> First, EA was polymerized to better than 95% conversion; then MMA was added to the EA emulsion polymer and also polymerized. This sequential polymerization of the monomers assures that large blocks of each of the monomers are formed. Small amounts of residual EA monomer can react with MMA monomer to form a small amount of alternating copolymer. The resulting polymer may be considered the product of an extreme compositional drift which is at the borderline of being a mixture of homopolymers.

### Procedure

The samples studied were all high-conversion emulsion polymers and are listed with their compositions in the accompanying tables. They were obtained as solids or emulsions. Emulsions were brought to dryness in a vacuum oven at 60°–80°C. Accurately weighed amounts of 1–2 mg were generally pyrolyzed at 450°C for 60 sec. The preliminary investigations

TABLE I  
Effect of Pyrolytic Temperature on the Recovery of Alcohol and Monomer

	350°C	375°C	400°C	425°C	450°C	475°C	500°C
Pol. 11—Homopolymer of EA							
EMA	— <sup>a</sup>	100	160	180	225	230	250
EA	220	950	950	1510	2150	1600	1700
EtOH	3200	9300	9300	10100	8575	9500	9030
Sum	3420	10350	13160	11790	10950	11330	10980
EtOH/EA	14.5	9.8	10.0	6.7	4.4	5.9	5.3
Pol. 2—Random Copolymer of 50/50 EA/MMA							
EMA	740	2230	1670	1770	500	1540	900
MMA	8900	9340	9500	11000	13000	11130	11820
EA	— <sup>a</sup>	2580	3180	3920	5040	3240	2900
MA	—	740	530	850	315	1150	1120
EtOH	1790	4030	2800	2700	1760	3360	2760
MeOH	950	2360	1630	1350	1320	1520	1300
Sum	12380	21280	19310	21590	21935	21940	20800
EtOH/EA	—	1.56	0.88	0.68	0.34	1.03	0.95
Pol. 4—Block Copolymer of 50/50 EA/MMA							
EMA	40	1200	1300	580	250	790	220
MMA	14740	19200	20850	21800	21280	22000	22300
EA	— <sup>a</sup>	—	610	870	1010	910	1030
EtOH	2020	6460	5440	4760	2980	4740	3860
MeOH	300	1770	1350	1060	350	740	60
Sum	17070	28650	29550	29070	25870	29180	27470
EtOH/EA	—	—	8.9	5.47	2.7	5.2	3.7

<sup>a</sup> Not detectable.

for alcohol and monomer recoveries were performed at different pyrolytic temperatures. These data are collected in Table I. Peak areas of the pyrolytic components were measured in mm<sup>2</sup>, normalized to unit sensitivity of the instrument and to 1-mg sample size. The thermal response factors of the major pyrolytic components, obtained by the injection of known quantities, were used to calculate their amount in the pyrolyzates. Elution times and abbreviations of selected pyrolytic components are given in the appropriate tables. The component data in the tables are the average values of three or more experiments.

### Apparatus

Separations were carried out with an Aerograph 202 gas chromatograph with dual-column, linear temperature programmer, W-type filaments detector with 200 milliamperes. A Burrell stainless steel boat pyrolyzer was attached to the injection port. The carrier gas was helium at a rate of 30 ml/min. Recorder: Leeds & Northrup 1 mv full scale, chart speed 1/2 inch/min. Temperatures: detector 260°, injection port 200°.

*Column A.* A 15 ft × 1/8 in. O.D. stainless steel column packed with 7.5 g 20% Carbowax 20M-TPA on Chromosorb-W 60/80 mesh was used to

separate components listed in Tables II, III, and IV. Column temperature was isothermal from 0–6 min at 80°, then programmed at 10°/min to 200°, isothermal after that.

*Column B.* A 9 ft  $\times$  1/8 in. O.D. column packed with 30/60 mesh silica gel, conditioned at 200°C for several hours, was used to separate CO<sub>2</sub>, alkanes, and olefins listed in Table V. Detector and injection temperatures are the same as with column A. Column temperature was 50° from 0–2.5 min, then programmed at 20°/min to 200°. Nongaseous components were trapped in a stainless steel U-tube, 12 in.  $\times$  1/8 in. O.D. partly filled with 30/60 mesh glass beads. The U-tube was attached between the pyrolyzer and the injection port, and was cooled with an acetone dry-ice mixture.

*Column C.* Same as column A, except only 3 ft long. It was programmed immediately from the moment of pyrolysis from 100° to 200°C at 10°/min.

## RESULTS AND DISCUSSION

### Pyrolytic Temperature

Earlier experience with the pyrolysis of acrylic polymers indicated that the alcohol and monomer yield varied with the temperature of pyrolysis. Therefore, a brief investigation was carried out to elucidate the effects of pyrolysis temperature on the yields of alcohol and monomer. Three different polymers were used: an EA homopolymer (Pol. 11), a random copolymer (Pol. 2), and a block copolymer of EA/MMA (Pol. 4). Data are collected in Table I.

Pyrolysis data showed that the major degradation products of ethyl acrylate homopolymer are ethyl alcohol, carbon dioxide, ethylene, and ethyl acrylate. Minor degradation products are ethyl acetate, ethyl methacrylate, acrylic acid, ethyl acrylate dimers, ethyl acrylate trimer (not eluted under present conditions), carbon monoxide, and ethane.

The amount of the major and minor degradation products varies with the pyrolysis temperature. At lower temperature (350°C), the relatively high ethyl alcohol yield gave the impression that EA degradation may start with the formation of alcohol while the other components are formed at higher temperatures and at a later stage of the degradation. Data in Table I may not show this convincingly, but data reported by others<sup>13,14</sup> show even higher alcohol production at lower pyrolytic temperatures. A short summary shows the following:

Author	Pyrol. temp.	% Alcohol	% Monomer	Ratio
Straus <sup>13</sup>	299–399°C	14.6 MeOH	0.7 MA	20
Grassie <sup>14</sup>	315°C	22.4 EtOH	0.3 EA	75
Grassie <sup>14</sup>	315°C	22.7 BuOH	0.2 BA	110
This work	350°C	6.0 EtOH	0.4 EA	15

It is surprising that the monomer was ever considered a "major" degradation product of an acrylate homopolymer at low temperatures. The

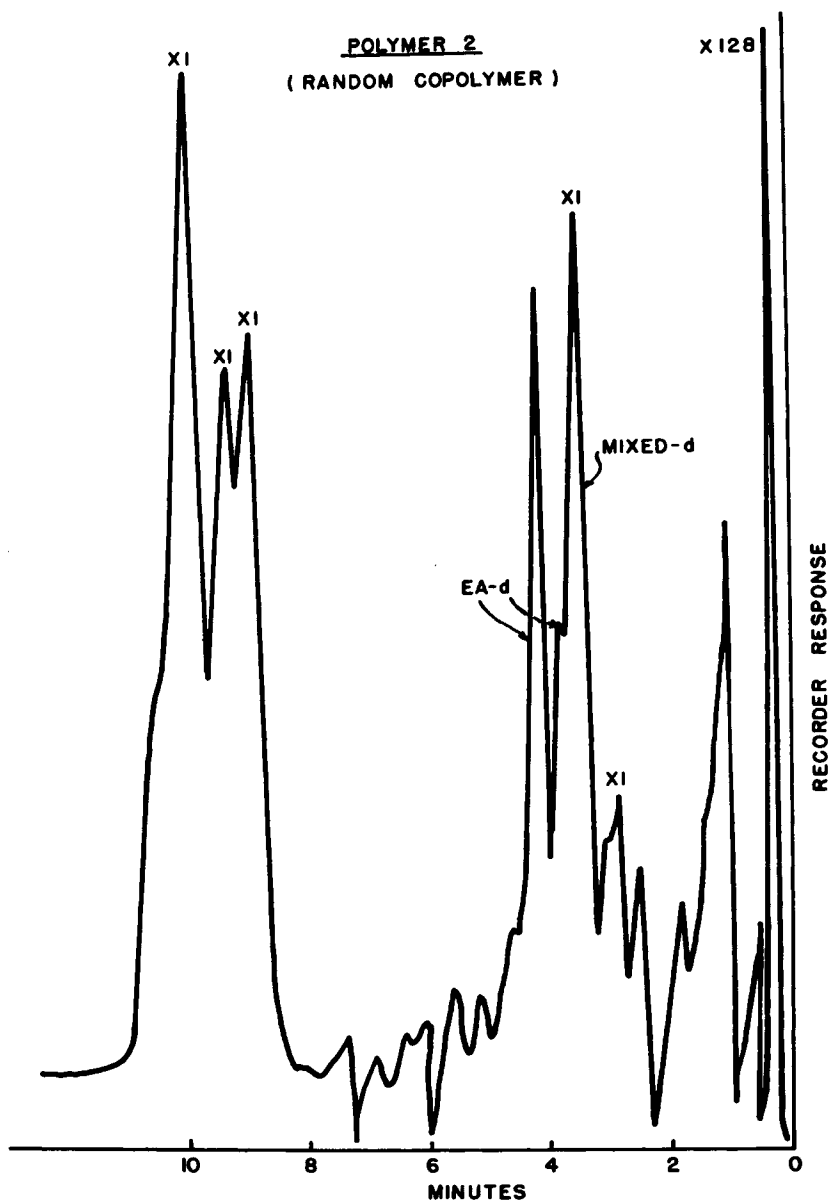


Fig. 1. Pyrogram of a random copolymer of 50/50 EA/MMA on column C.

alcohol to acrylate ratio improves with increasing pyrolytic temperatures. Further, the ethyl alcohol and ethyl acrylate monomer yields apparently compensate for each other, for the sums of alcohols and monomers recovered are fairly constant between 375° and 500°C. The standard deviations of the sums of alcohols and monomer for the three polymers are: Pol. 2 = 4.4%, Pol. 4 = 4.8%, Pol. 11 = 8.5%. In contrast to the small deviations

of the sums of alcohol and monomer, the *ratios* of EtOH/EA yields show large differences at different temperature. The yields and the ratios are characteristic of the mode of polymer preparation, even at different pyrolytic temperatures. The yields of CO<sub>2</sub> and ethylene are functions of the

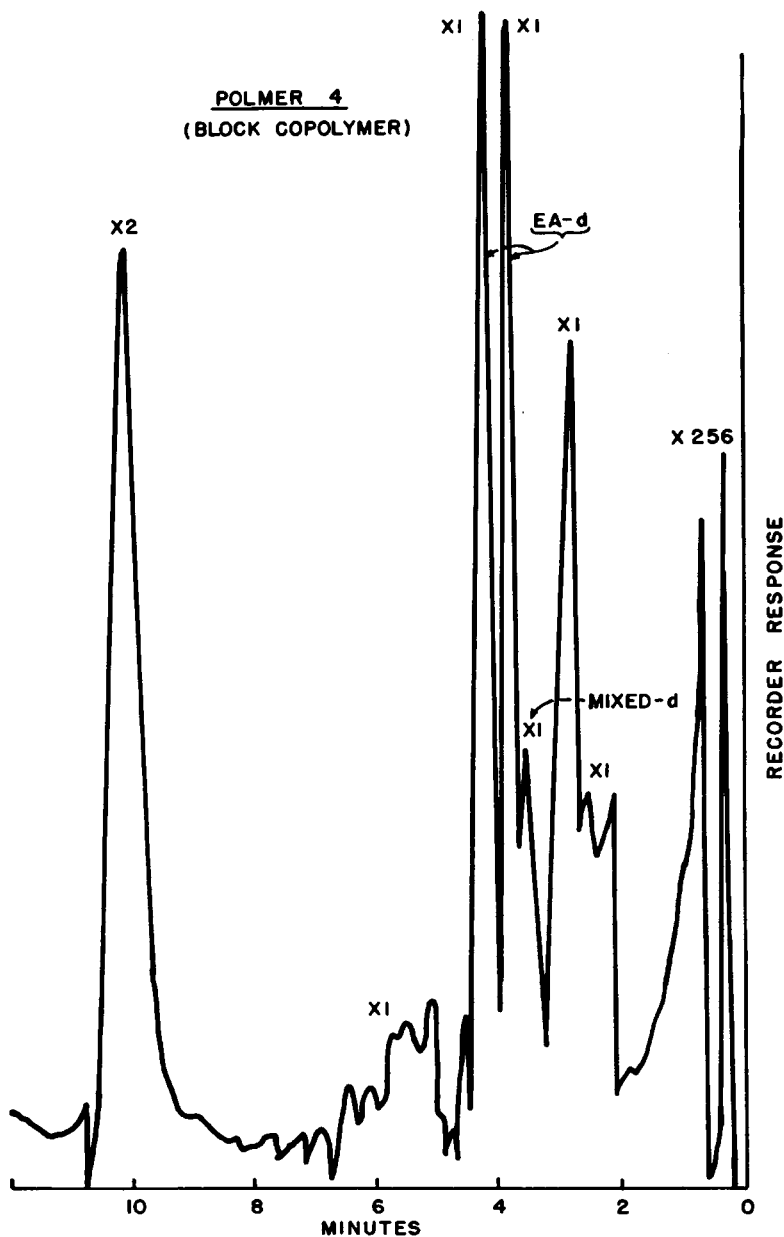


Fig. 2. Pyrogram of a block copolymer of 50/50 EA/MMA on column C.

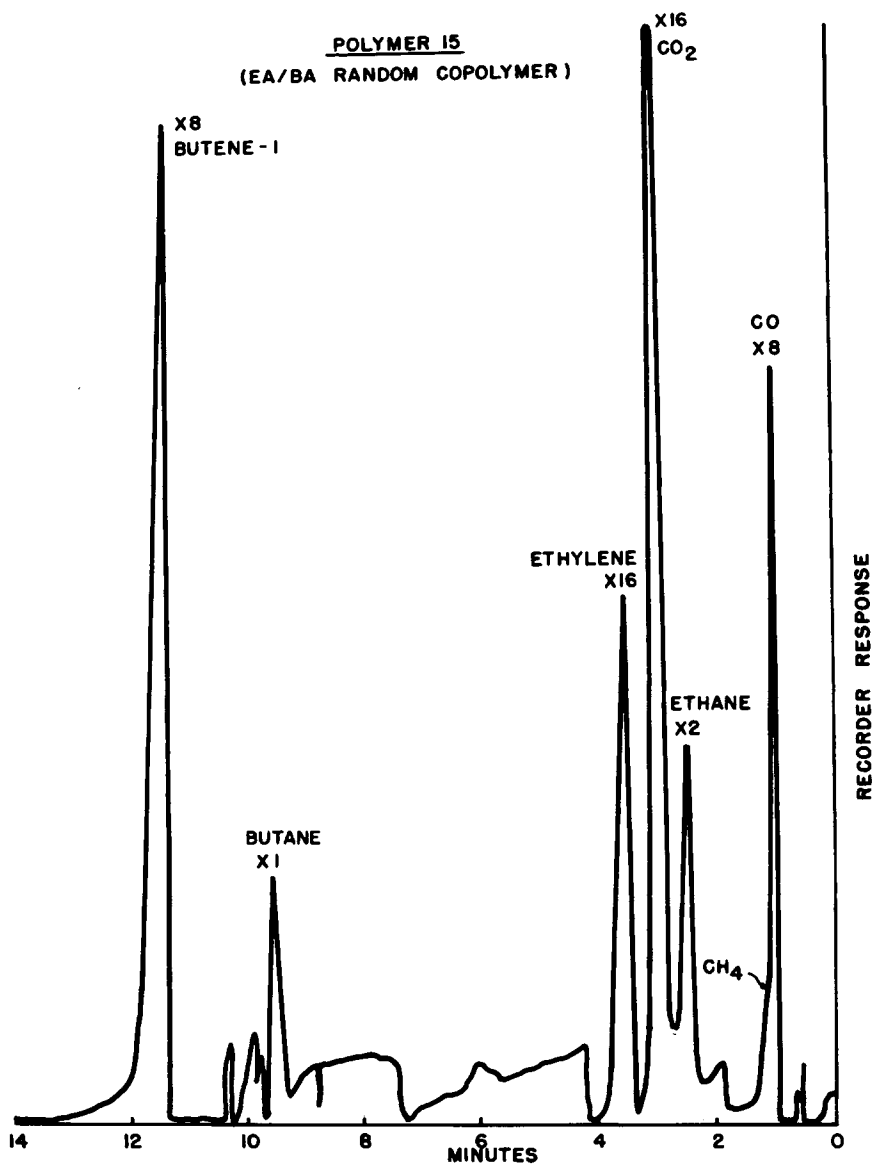


Fig. 3. Pyrogram of a random copolymer of 50/50 EA/BA on column B.

pyrolytic temperatures and cannot be related to the mode of polymer preparation. These data are therefore omitted from Table I.

The overall evaluation of the pyrograms for homo- and copolymers showed that 450°C offers a good yield of the major and minor degradation products useful for polymer characterization. Even under optimum conditions, approximately 50% of the pyrolyzed sample cannot be recovered, for it is lost either as nondegraded residue, or it is not eluted under the con-





EMA	10.2							126	
MMA	9.2	345			47950			772	
EA	8.6	32		2150				4410	
MA	7.0	1920		8575				5280	
EtOH	6.2							10560	
MeOH	5.2	7476						3100	
1-Butene	1.2		8450		9800			1376	
Olef. + CO <sub>2</sub>	1.1	6700 <sup>a</sup>	5290		4280		1030	48766	
Sum of all peaks		17473	27350	26270	26915	49110	47410	27680	
				Recovery of, %					
Olefin		1.1 <sup>a</sup>	16.0	12.3	18.6	5.4	5.4	8.5	10.0
CO <sub>2</sub>		13.0	10.0	12.3	8.2				
Alcohol		15.8	11.7	16.3	15.0				17.5
Monomer		4.0	8.0	4.1	4.7	93.6	87.0	80.0	6.0
Sample		37.4	53.0	51.6	52.6	99.4	92.4	93.5	54.0
				Ratios					
MeOH/MA		3.9							
EtOH/EA				4.0					5.7
BuOH/BA			1.5		3.2				5.7

<sup>a</sup> This component is CH<sub>4</sub> in Pol. 19.

ditions used with column A. It was possible to show late eluting components under the conditions used with column C (Figs. 1 and 2). They have not been identified, but still can be used to distinguish between random and block copolymers of 50/50 EA/MMA.

### CO<sub>2</sub> and Olefin

Column B was used to separate the 1.1 minute peaks. These peaks consist of CO, methane, ethane, ethylene, and CO<sub>2</sub>. They are tabulated for selected polymers in Table V. A typical separation of these components on Column B can be seen in Figure 3. The areas of the unresolved 1.1 minute peaks listed in Table II are very comparable to the sums of the areas of the separated components. The CO<sub>2</sub> and ethylene yields are independent of the type of copolymer (homo-, block, or random) and apparently originate only from the acrylate moiety of the copolymers. Data in Table III shows that ethylene is produced in almost equal amounts in random and block copolymers with 50/50 EA/MMA ratios. Table V shows that the

TABLE III  
Component Intensities of Random and Block Copolymers

Component	Elution time, min	Random copolymers of EA/MMA*				Block copolymers of EA/MMA	
		Pol. 8 55% EA	Pol. 5 51% EA	Pol. 1 50% EA	Pol. 2 50% EA	Pol. 3 50% EA	Pol. 4 50% EA
EA	26.7	480	266	390	390	510	580
doublet	24.8	270	170	244	170	464	520
Mixed	24.0	205	170	200	290	88	80
doublet	23.2	105	160	150	200	16	20
Sum of doublets		1060	766	984	1050	1078	1200
		Ratio of EA doublet/Mixed doublet					
		2.4	1.0	1.8	1.1	9.7	11.0
MAA	21.0	400	112	135	187	140	250
AA	20.0	165	324	126	170	95	55
EMA	10.2	610	513	1040	500	424	253
MMA	9.2	10250	10480	13440	13000	19047	21280
EA	8.6	4080	4180	4460	5040	1400	1010
MA	7.0	170	230	280	313	78	40
EtOH	6.2	3020	2210	1240	1760	3070	2975
MeOH	5.2	1550	1600	900	1320	684	350
Olef.	1.1	8480	7680	5712	6000	7343	6480
				Sum of all peaks			
		29785	27334	28417	29340	33359	33893
		Recovery, %					
		54.0	53.5	55.0	57.0	65.0	65.5
		EtOH/EA Ratio					
		0.56	0.52	0.27	0.34	2.2	3.0

\* The amount of MMA is 100 - % EA.

TABLE IV  
Component Intensities of Terpolymers with Different EA/MMA Ratios<sup>a</sup>

	86/09/5 Pol. 6/a	75/20/5 Pol. 7	55/40/5 Pol. 8	45/50/5 Pol. 8/a	45/55/5 Pol. 8/b	20/75/5 Pol. 9	9/86/5 Pol. 9/a
MAA	160	250	400	530	620	720	780
EMA	640	470	1170	640	880	600	360
MMA	1330	4310	10250	16200	17900	31200	38200
EA	2900	3660	4080	4670	4630	3500	1700
MA	—	70	170	460	520	180	130
EtOH	7830	7000	3020	2050	1650	600	350
MeOH	450	1200	1530	1290	1330	820	650
Olef.							
CO <sub>2</sub>	13010	11200	8480	7750	7420	4350	3110
EtOH/EA	2.70	1.90	0.74	0.44	0.36	0.17	0.21

<sup>a</sup> The compositional ratio is in the order EA/MMA/MAA.

CO<sub>2</sub> yield is almost the same in MA, EA, and BA homopolymers and that the olefin yields from EA and BA are nearly equal. These data also support the proposition that olefin and CO<sub>2</sub> production arise from the same mechanism. Comparing the CO<sub>2</sub> yields of the different acrylates (Table V), we found a standard deviation from their average value of only 10%. The small deviation emphasizes even more that the CO<sub>2</sub> production is independent of compositional variables. The contribution of methacrylates to the CO<sub>2</sub> yield is negligible. The sum of CO<sub>2</sub>, olefin, and alcohol is about 80% of the total recovered degradation products of acrylates, but only 5–6% of the methacrylates.

### Methyl Methacrylate (MMA) and Methyl Alcohol (MeOH)

While p-MMA homopolymer usually gives a 95% or better monomer recovery on pyrolysis, in block copolymers of 50/50 EA/MMA composition the MMA recovery is down to about 77%, and in random copolymers it is only about 44% of the MMA present in the polymer (Tables II, III). As the MMA recovery decreases from homo- to block to random copolymers, MeOH does the opposite. It never reaches the high yields of ethanol, but increases significantly in the random copolymers (randomness reaching a maximum in the copolymer with about equal amounts).

### Methacrylic Acid

Some of the polymers investigated contain methacrylic acid. It is an elusive component in pyrolysis. As can be seen in Table IV, the recovery of the 5% copolymerized MAA as monomer increases with increasing MMA present in the terpolymer. The presence of the 5% copolymerized MAA apparently did not influence the kind or amount of the other pyrolytic products of the polymers involved.

### Methyl Acrylate (MA)

Although methyl acrylate has not been observed in measurable quantities among the degradation products of p-MMA homopolymer, it is defi-

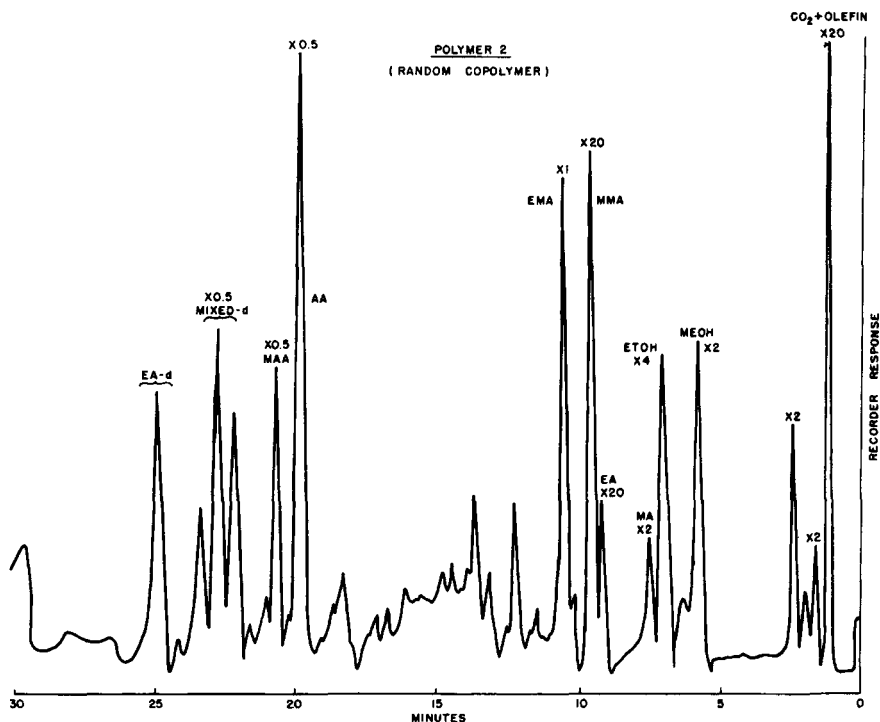


Fig. 4. Pyrogram of a random copolymer of 50/50 EA/MMA on column A.

nitely present in the pyrolyzates of the copolymers of EA/MMA. Table III shows that the random copolymers of EA/MMA yield about four times more pyrolytic MA than their block copolymer counterparts (see Figs. 4 and 5 for random and block copolymers). Strassburger,<sup>15</sup> Grassie and Torrance<sup>4</sup> and Gatrell and Mao<sup>10</sup> report that MA monomer production was found larger in a copolymer of MA/MMA than was expected from the degradation behavior of p-MA. It can now be shown that, first, the "extra" amount of pyrolytic MA comes from the more complete depolymerization of an acrylate (in this case MA) to the monomer in random copolymers relative to block and homopolymers. Second, some contribution to the "extra" MA yield can also be expected from the degradation of a few MMA molecules, since the presence of MA in the pyrolyzates of our EA/MMA copolymers must be the result of a breakdown of certain MMA molecules to MA units. Copolymers listed in Table IV show again that a larger monomer yield is always associated with a smaller alcohol yield.

### Eethyl Methacrylate (EMA)

Eethyl methacrylate, present in the pyrolyzates of EA homopolymers (Table II), shows about a twofold increase in the pyrolyzates of the random copolymers (Table III) when the EMA is expressed relative to the amount

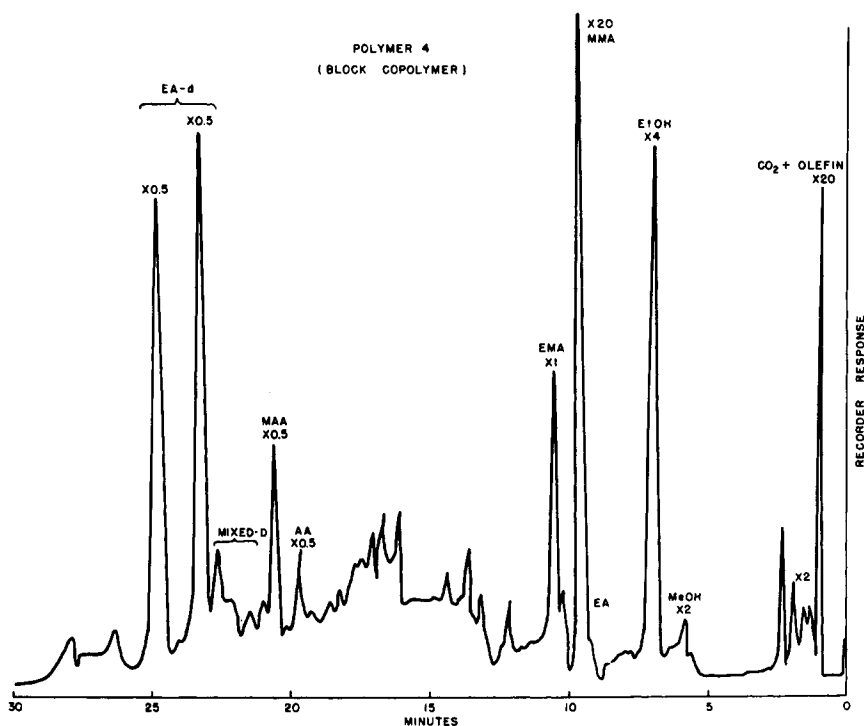


Fig. 5. Pyrogram of a block copolymer of 50/50 EA/MMA on column A.

of copolymerized EA. The yields of EMA increase in the order homopolymer < block copolymer < random copolymer. Thus, the more uniform the EA/MMA distribution, or the less pronounced the block character, the more EMA and MA is generated on pyrolysis. It was also observed that not only the pyrolyzates of p-EA contain the methacrylate counterpart EMA, but that the pyrolyzates of the other acrylates also contain the corresponding methacrylate. Thus, MA homopolymer shows the presence of MMA and butyl acrylate (BA) that of butyl methacrylate (BMA). The methacrylates (MMA, EMA, BMA) show their acrylate counterparts only when they are in a random copolymer with an acrylate.

### Dimers and Mixed Dimers

Two late-eluting components were detected in the pyrolyzates of the homopolymers of EA, MA, i-BA, and BA. They are the corresponding dialkyl glutarate and the dialkyl  $\alpha$ -methylene-glutarate, respectively. (In the pyrogram of BA, there was a third component found; it has not been identified yet.) These two components arise from two monomer units of the degraded polymers and are called arbitrarily the EA-doublet, MA-doublet, etc. These doublets have the same intensity in the individual homopolymers as in their mixed homopolymers. Mixed homopolymers of EA/MMA show only the EA-doublet since p-MMA decomposes virtually

to the monomer. The dimer of MMA (dimethyl  $\alpha$ -methylene- $\alpha'$ , $\alpha'$ -dimethylglutarate) elutes after the EA doublet and has not been observed in measurable quantities. In *block copolymers* of EA/MMA the major doublet is that of EA. Two smaller components are the *mixed doublets* (EA/MA) containing an EA and an MMA residue which lost the methylene group connecting it to the next polymer unit. This mutilated MMA is now an MA unit. The intensity ratios of EA doublet/mixed doublets in block copolymers is about 10 (Table III). In *random copolymers* of EA/MMA, the ratios of EA doublet/mixed doublets is about 1.6, a sixfold increase of the mixed doublets.

The sums of the four components of the doublets are listed in Table III. In spite of the ratio differences, these sums are relatively constant. This indicates that the increase of the mixed doublets in the random copolymers occurs primarily at the expense of the EA doublets, since there are more alternating EA/MMA/EA/MMA sequences in the random than in the block copolymers. Therefore, the presence or the absence of the mixed doublets (EA/MA) is again an indication of random or block copolymerization. Typical pyrograms of a random (Pol. 2) and a block (Pol. 4) copolymer can be seen in Figures 4 and 5.

Although our primary interest in these experiments was in EA/MMA copolymers, the random copolymer of EA/BA (Pol. 15) should be mentioned, for it provides us with EA doublets, EA/BA mixed doublets, and BA doublets. The presence of the EA/BA mixed doublets is so far the only clue to random copolymerization of two acrylates. The pyrolyzates of the physical mixtures of EA and BA, or EA and MA do not produce the corresponding mixed doublets. Because of the lack of acrylate/acrylate *block* copolymer, we can only assume that, when pyrolyzed, a block copolymer will produce much less, if any, mixed doublets than a random copolymer. (See Table V.)

### Alcohol and Acrylate

The abundance of alcohol in the pyrolyzates of acrylates and the virtual absence of it in the methacrylates was one of the earliest observations. As the yields of alcohol and monomer were compared in the pyrolyzates of the different polymers, it was found that the sums of EtOH + EA, MeOH + MA and BuOH + BA showed an amazingly close average value of 21% when the amount of alcohol + acrylate is expressed as the percentage of the amount of copolymerized acrylate in any given sample. For example, Pol. 7 (Table VI) would show the following:

$$\begin{aligned} \% \text{ EA} &= \frac{0.056 \text{ mg EA recovered}}{0.75 \text{ mg EA in 1 mg polymer}} \times 100 = \frac{5.55}{0.75} = 7.4\% \\ \% \text{ EtOH} &= \frac{0.100 \text{ mg EtOH recovered}}{0.75 \text{ mg EA in 1 mg polymer}} \times 100 = \frac{10}{0.75} = 13.4\% \end{aligned}$$

The sums of the two percentages = 20.8%

TABLE V  
Separation of the 1.1 Minute Peaks of Selected Polymers on Column B<sup>a</sup>

Compound	Elution time, min	Pol. 19	Pol. 11	Pol. 16	Pol. 4	Pol. 18	Pol. 15
		MA homopol.	EA homopol.	BA homopol.	EA/ MMA block	BMA homo- pol	EA/BA Random
Butene	11.2	—	—	6440 <sup>b</sup>	—	2750	3150
Butane	9.5	—	—	130	—	24	170
Ethylene	3.4	—	6270	—	2360	—	2800
CO <sub>2</sub>	2.9	4850	5950	4080	3200	756	5800
Ethane	2.4	—	220	60	60	—	145
Methane	1.1	560	—	—	—	—	—
CO	1.0	460	980	680	500	120	720
Sum of peak areas		5870	13420	11390	6120	3650	12785
Area of the 1.1 minute peak from Table III		6700	13440	14080 <sup>c</sup>	6480	4476	15840

<sup>a</sup> Conditions described in the experimental section.

<sup>b</sup> Area intensities are in mm<sup>2</sup> at unit sensitivity per mg sample.

<sup>c</sup> Areas include 1-butene also.

TABLE VI  
Percent Recovery of Acrylates and Alcohols

Polymer	Polymer type	Acrylate in polymer, %	Recovered, %			
			Acrylate	Alcohol	Total	
Pol. 1	random	50 EA	17.00	4.75	21.75	
Pol. 2	random	50 EA	19.20	6.70	25.90	
Pol. 5	random	50 EA	15.70	8.20	23.90	
Pol. 3	block EA first	50 EA	5.35	11.70	17.05	
Pol. 4	block MMA first	50 EA	3.84	11.30	14.14	
Pol. 6	random	95 EA	4.37	18.20	22.57	
Pol. 6a	random	86 EA	5.60	15.10	20.70	
Pol. 7	random	75 EA	7.42	13.40	20.82	
Pol. 8	random	55 EA	14.20	8.00	22.20	
Pol. 8/a	random	45 EA	17.30	7.50	24.80	
Pol. 9	random	20 EA	24.00	4.30	28.30	
Pol. 11	homopolymer	100 EA	4.10	16.40	20.50	
Pol. 13	random	87 EA	3.00	17.50	20.50	
Pol. 14	random	87 EA	4.20	15.50	19.70	
Pol. 15	random	50 EA	3.10	17.50	20.60	
Pol. 15	random	50 BA	3.10	17.50	20.60	
Pol. 16	homopolymer	100 BA	4.70	15.00	19.70	
Pol. 17	homopolymer	100 i-BA	8.00	11.65	19.65	
Pol. 19	homopolymer	100 MA	4.04	15.80	19.84	
Pol. 21	mixed homopol.	100 MA	4.50	19.00	23.50	
Pol. 21	mixed homopol.	100 EA	4.20	16.20	20.40	
Strauss <sup>13</sup>	homopolymer	100 MA	0.70	14.60	15.30	
Chitoku <sup>16</sup>	homopolymer	100 MA	6.70	16.20	22.90	
Grassie <sup>14</sup>	homopolymer	100 EA	0.32	22.40	22.72	
Grassie <sup>14</sup>	homopolymer	100 BA	0.20	20.70	20.90	
					Average	21.16

The polymers listed in Table VI are different in either the type of the acrylate, composition of the polymer, method of preparation, or the presence of 5% copolymerized methacrylic acid. Apparently, none of these differences influenced the sum of the acrylate and alcohol recoveries. Table VI shows comparable results obtained by other authors.

When the *alcohol to acrylate ratios* ( $R = \text{EtOH/EA}$ ) were summarized (Tables II, III, IV), it was found that the ratios are much larger in the homo- and block copolymers than in the random ones. That is to say, homopolymers show ratios between 3 and 5, block copolymers, between 2 and 3, but random copolymers, between only 0.2 and 0.5. The ratios are characteristic of the mode of polymer preparation.

The reversal of the alcohol to monomer yield of the acrylate moiety of the random copolymer (containing about equal amounts of EA and MMA) is due to the alternating EA and MMA molecules, or to the short EA and MMA blocks alternating within the long polymer chain in contrast to block- or homopolymers where long blocks of the individual EA and MMA molecules make up the polymer chain. Just what is the smallest EA block which still can produce ethyl alcohol is an intriguing question. The high-conversion random copolymers used in these experiments are obviously not suited to answer this question, because some block character is present in them due to compositional drift. These experiments did not intend to find out whether alcohol production can be related to diads, triads, tetrads, etc., of EA units. Results obtained by Grassie<sup>4</sup> indicate that sequences of at least three acrylate units are necessary for the evolution of alcohol, because no detectable amount of methanol was found in a 2:1 MMA/MA low-conversion (about 5%) copolymer. This suggests again that the low yield, or even the absence, of alcohol is the result of an ideal acrylate/methacrylate sequence distribution.

Although the alcohol is the largest pyrolytic product of acrylate homopolymers, it has never been found more than about 22% by weight of the initial polymer. As the long EA polymer chains are more and more interrupted by copolymerized MMA, there will be a decreasing amount of ethyl alcohol (and increasing amount of ethyl acrylate) produced per EA content of the copolymer. Data in Table IV show a set of random copolymers where this phenomenon can be observed. Naturally, this results in the corresponding changes of the alcohol-to-monomer ratios which now show some correlation to EA polymer block length, the latter being shortened by the decreasing EA moiety in the copolymers. It can be shown that 20% EA content in a copolymer (Pol. 9) generates 3.6 times more EA monomer on pyrolysis per EA content of the polymer than 75% EA content (Pol. 7, Table IV). Data reported by Ferlauto et al.<sup>9</sup> and McCormick<sup>5</sup> are comparable with our results. This observation is apparently valid with BA/MMA copolymers also. A short summary of these data is shown in Table VII.

Unfortunately, the above authors<sup>5,9</sup> do not report alcohol recoveries of their copolymers. In our samples, decreasing EA content in the copoly-



TABLE VII  
Monomer Yields of Copolymers with Low and High EB Contents

Sample		Relative amount of EA Fraction EA	Yield from low EA polymer Yield from high EA polymer
	<u>EA/MMA</u>		
Polymer 9	20/75	$\frac{3.50 \times 10^3 \text{ mm}^2}{0.20} = 17.5$	$\frac{17.5}{4.9} = 3.6$
Polymer 7	75/20	$\frac{3.66 \times 10^3 \text{ mm}^2}{0.75} = 4.9$	
Sample 8 Ferlauto et al. <sup>9</sup>	20/80	$\frac{10.54 \times 10^3 \text{ counts}}{0.20} = 53.0$	$\frac{53.0}{15.1} = 3.5$
Sample 5	80/20	$\frac{12.07 \times 10^3 \text{ counts}}{0.80} = 15.1$	
McCormick <sup>5</sup>	25/75	67.0% EA recovery	$\frac{67.0}{15.4} = 4.3$
	80/20	15.4% EA recovery	
	<u>BA/MMA</u>		
McCormick <sup>5</sup>	20/80	36.4% BA recovery	$\frac{36.4}{11.4} = 3.2$
	80/20	11.4% BA recovery	

mers results in decreasing amounts of ethanol in the pyrolyzates (Table IV). It can be shown that 20% EA content in a random copolymer (Pol. 9) generates 3.1 times less ethanol than 75% EA content (Pol. 7).

Dandoy and Deneubourg<sup>11</sup> observed, without further elaborating, that there was a reversal of the pyrolytic alcohol to monomer yield when a low-conversion random copolymer with equal amounts of EA/MMA was compared to a high-conversion counterpart manufactured on a factory scale. Since they originally reported the ratios as monomer to alcohol, we expressed them in reciprocal terms as alcohol to monomer, as we have done in Table III. The ratios now show that the low-conversion copolymer has an EtOH/EA value of 0.27, and the high-conversion copolymer of 1.35. The five times more alcohol in the high-conversion sample can be correlated with the presence of large blocks of EA polymer (the result of compositional drift during polymerization) which permitted the formation of large amounts of alcohol, just as was observed in EA/MMA block copolymers and, of course, in EA homopolymers.

In acrylate/acrylate random copolymers, there is no alcohol-to-acrylate ratio reversal as is found in acrylate/methacrylate random copolymers. A random copolymer of EA and BA (Pol. 15, Table II) shows the alcohol-to-acrylate ratio for EA and BA as if the sample were a mixture of the homopolymers. The only way we know that the sample is a random copolymer is that the EA/BA mixed doublets appear along with EA doublets and BA doublets.

Whatever the actual degradation mechanism leading to ethanol and acrylate may be, one cannot fail to note the presence of a limiting or govern-

ing factor. While the pyrolytic temperature has already been noted as a controlling factor, at a given temperature the amounts are further influenced by the type of polymer (homo- or copolymer), the mode of copolymer preparation (random, block, low or high conversion), the amounts of EA and MMA in the copolymers, and their reactivity ratios. These factors can all be reduced to differences in the sequence distribution of acrylate and methacrylate molecules. That is to say, as long as the uniformity of acrylate and methacrylate sequences, or the "randomness" of the copolymer is maintained (by avoiding block formation via the compositional drift during polymerization), the yield of alcohol is zero, or minimal at best, and the yield of the monomer and mixed doublets is maximal.

Once the copolymer is prepared, it apparently does not matter whether it was made in an aqueous phase or in solution, or as a bulk in dilatometers under vacuum; whether the inhibitor of the monomer or the plasticizer was removed; what type of initiator was used for the polymerization; whether the emulsion polymerization was redox or reflux type; or whether the polymer was further purified prior to pyrolysis.

Because in these experiments the samples were all high-conversion copolymers, no attempt was made to calculate sequence distribution. Ferlauto et al.<sup>9</sup> have shown that there is good correlation between ethyl acrylate yield and sequence distribution data for low-conversion copolymers, in which the fraction of A—B bonds remains the same as the copolymer composition is varied. They have also shown some discrepancies with this correlation in high-conversion copolymers and pointed out that this may be due to the compositional drift existing in high-conversion copolymers as the result of differences in the reactivity ratios of EA and MMA.

In conclusion, it can therefore be said that the *alcohol* production of acrylate *decreases* (and that of the *monomer increases*), going from homopolymers to block copolymers to high-conversion random copolymers and to low-conversion random copolymers.

The block or random character of a given high-conversion copolymer containing about equal amounts of ethyl acrylate and methyl methacrylate can be judged from the relatively high (H) or low (L) yields of the following pyrolytic components:

Yield	Block copolymer	Random copolymer
(1) EA monomer	L	H
(2) EtOH	H	L
(3) EtOH/EA ratio	H	L
(4) EA doublets	H	L
(5) Mixed doublets	L	H
(6) Acrylate yield of the methacrylate moiety	L	H
(7) Methacrylate yield of the acrylate moiety	L	H
(8) MeOH	L	H
(9) MMA monomer	H	L

The production of alcohol requires the availability of a hydrogen. This hydrogen may very well be the tertiary hydrogen of the acrylates, since it is the easiest to abstract by the electronegative alkoxy oxygen. The availability is apparently different in random and block copolymers of acrylates with methacrylates. Therefore, we may assume first, that the tertiary hydrogen is not abstracted by the alkoxy oxygen of the same molecule, otherwise the alcohol yields of random and block copolymers would not be so different; second, that the availability depends on the proximity of the tertiary hydrogen and the alkoxy oxygen; and third, that the proximity is determined by the sequence distribution of acrylate and methacrylate molecules, which in turn is the result of the mode of polymer preparation. The availability of the tertiary hydrogen and the consequent high alcohol production is clearly demonstrated in the random copolymer of two acrylates EA and BA (Table II, Pol. 15).

Methacrylates make much less use of the available tertiary hydrogen, even though the proximity of the tertiary hydrogen and the alkoxy oxygen of a methacrylate may favor abstraction. Table III shows that the amount of MeOH formed in random copolymers is about 2.5 times larger than in the corresponding block copolymers. It is apparently still easier to unzip MMA molecules to the monomer than to abstract a tertiary hydrogen via a methoxy group.

The role of the tertiary hydrogen could probably be clarified by the preparation and subsequent pyrolysis of an EA homopolymer having tritium in place of the tertiary hydrogen. The collected ethanol should show radioactivity if it is formed by abstraction of the tertiary hydrogen.

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### References

1. E. A. Radell and H. C. Sturz, *Anal. Chem.*, **31**, 1890 (1959).
2. E. M. Barrall, R. S. Porter, and J. F. Johnson, *Anal. Chem.*, **35**, 73 (1963).
3. K. J. Bombaugh and C. E. Cook, *Anal. Chem.*, **35**, 1834 (1963).
4. N. Grassie and B. J. D. Torrance, *J. Polym. Sci. A-1*, **6**, 3303 (1968).
5. H. McCormick, *J. Chromatogr.*, **40**, 1 (1968).
6. D. Noffz and W. Pfab, *Z. Anal. Chem.*, **228**, 188 (1967).
7. J. C. Daniel and J. M. Michael, *J. Gas Chromatogr.*, 437 (1967).
8. G. G. Cameron and D. R. Kane, *Makromol. Chem.*, **113**, 75 (1968).
9. E. C. Ferlauto, M. K. Lindemann, C. A. Lucchesi, and D. R. Gaskill, *J. Appl. Polym. Sci.*, **13**, 445 (1971).
10. R. L. Gatrell and T. J. Mao, *Anal. Chem.*, **37**, 1294 (1965).
11. J. Dandoy and C. Deneubourg, *J. Chromatogr.*, **56**, 126 (1971).
12. *Emulsion Polymerization of Acrylic Monomers*, Technical Bulletin CM-104 E/cd, Rohm and Haas Company, Philadelphia, Pennsylvania, 19101 (1970).

13. S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand.*, **50**, 165 (1953).
14. N. Grassie and J. G. Speakman, *J. Polym. Sc. A-1*, **9**, 931 (1971).
15. J. Strassburger, G. M. Brauer, M. Tyron, and A. F. Forziati, *Anal. Chem.*, **32**, 454 (1960).
16. K. Chitoku and H. Baba, *J. Chem. Soc. Japan. Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **61**, 865 (1958).

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