AD-A183 135 RESIST ROLYMERS 8 THERMOLYSIS OF BROMINE CONTAINING ACRYLATE POLYMERS(U) MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND ENGINE.. P K DHAL ET AL. JUN 87 1/1

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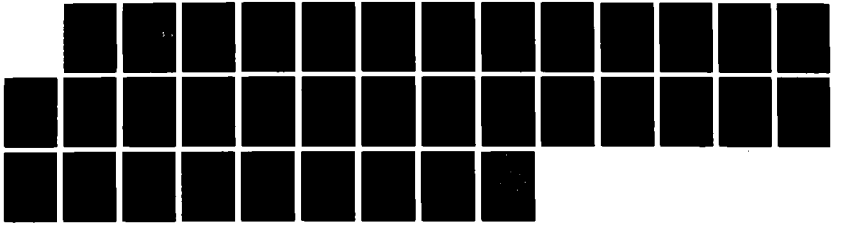

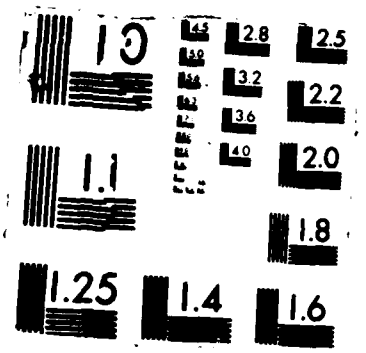
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Technical Report No. 3

Resist Polymers VIII.

Thermolysis of Bromine Containing Acrylate Polymers

by

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INTRODUCTION

Thermal decomposition of synthetic polymer can exclude its usage in certain applications.[1] It is often found that the thermal decomposition of polymer can differ significantly from those of model compounds because the chain environment may modify reaction pathways. The thermolysis of bromine containing polymers is particularly interesting because of their role as proven flame retardants. The bromine containing polymers behave differently from the fluorine and chlorine analogs toward energetic radiation[2-5] as possible candidates for positive electron beam resists. The radiolysis of bromine derivatives have marked tendency toward crosslinking, whereas fluorine containing polymers undergo only main chain scission. Theraml stabilities of these polymers are also important in this application because the requirements to withstand various heat treatment during the manufacturing of VLSI devices. In the previous paper of this series the principal features and products of thermal degradations of various fluorine containing poly(alkyl methacrylates) were described. Recently Grassie et al.[6] reported the thermal degradation of poly(2-bromoethyl methacrylate), PBEMA, and blends of PBEMA and poly(methyl acrylate) producing mainly monomer with small amounts of vinyl bromide and carbon dioxide. The central objective of this work is to identify the pyrolysis products of three bromine containing acrylate polymers and their copolymers with MMA and to understand the mechanism of

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thermal decomposition as compared to that for radiolysis. A further objective is to understand the differences between the thermolysis of bromine and fluorine containing polymers.

EXPERIMENTAL

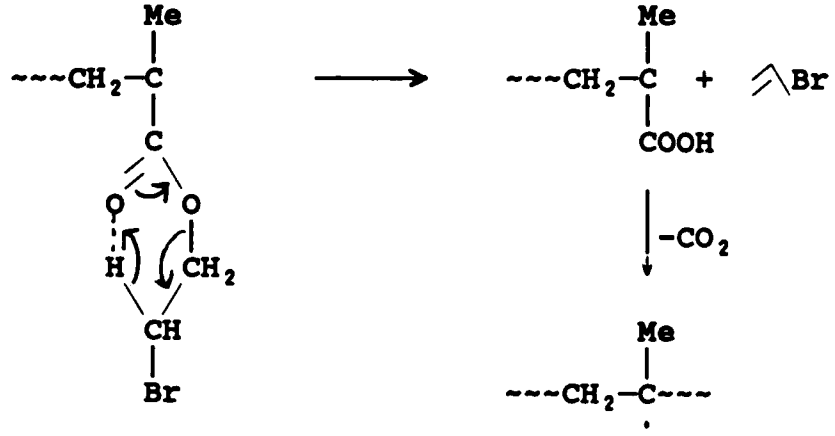
The monomers were synthesized and purified as described previously. MMA (Aldrich Chemical Co.) was dried over calcium hydride. Monomers were distilled under vacuum before polymerization. The polymers and copolymers were prepared in bulk as described previously.[2]

Thermogravimetric analysis was obtained with a Perkin-Elmer Thermobalance in N_2 atmosphere. Pyrolysis of polymers was performed as described earlier.[6]

RESULTS AND DISCUSSION

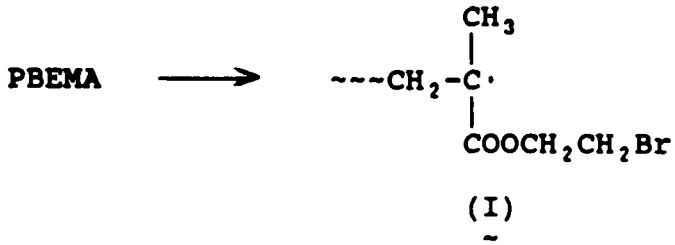
Poly(2-bromoethyl methacrylate) (PBEMA): the TGA curve of PBEMA, illustrated in Figure 1, shows two distinct stages of weight loss: the first stage is very slow, decomposing only about 8 wt % of the polymer at 225°, followed by a much faster weight loss with a maximum rate at 319° (Table I). The pyrogram of PBEMA is shown in Figure 2. The major products of pyrolysis are CO_2, vinyl bromide and ethyl bromide; amongst the minor products acetaldehyde, methyl bromide and methyl methacrylate are found in greater abundance (Table II). These are the products of ester decomposition and random main chain scission. Grassie et

al.[7] had proposed a six membered ring involving ß-hydrogen atoms as the intermediate for the formation of vinyl bromide and CO_2 from poly(t-butyl methacrylate),[8]



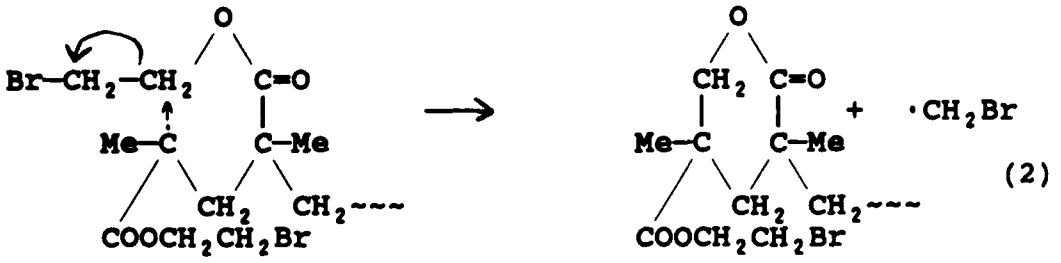
(1)

The presence of bromine on ester units apparently alters the principal mode of degradation of the parent poly(ethyl methacrylate)[7] which depolymerizes after undergoing main chain scission. In contradistinction, the main chain radical of PBEMA also undergoes inter- and intramolecular eliminations of alkyl bromides radicals. Elimination of $BrCH_2\cdot$ is illustrated by the following equations:



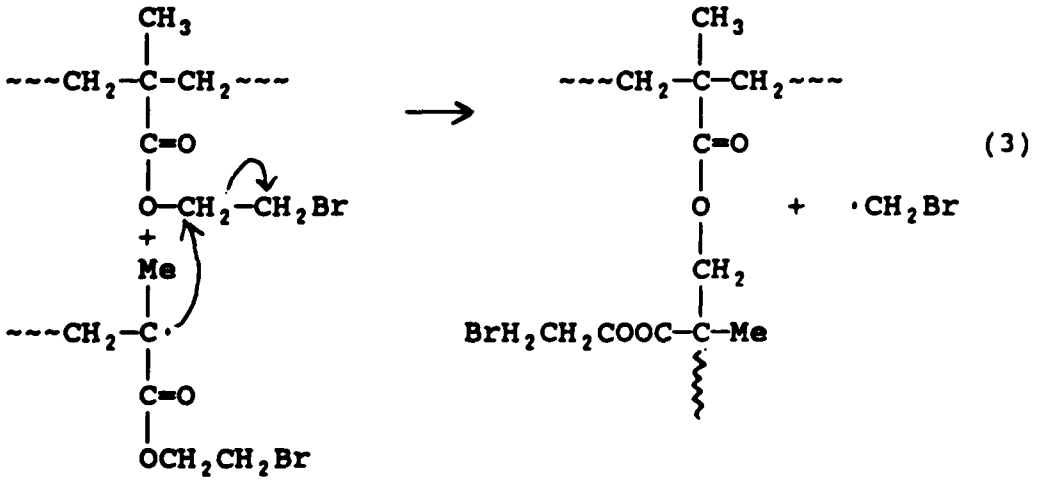
(I)

Intramolecular



(2)

Intermolecular

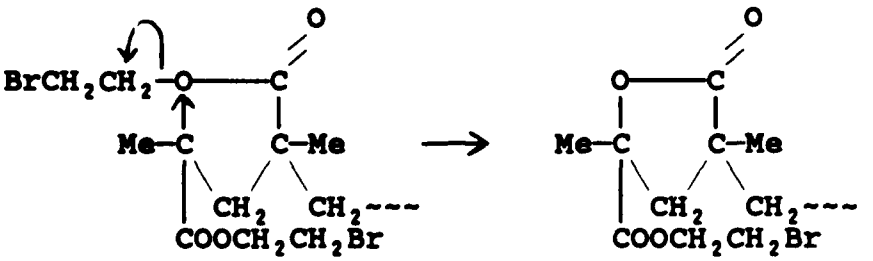


(3)

It is worthy of noting that the dimerization product of $BrCH_2\cdot$ was not found; probably at elevated temperatures 1,2-dibromoethane is unstable and readily dissociates. The intramolecular reaction can be justified on the basis of molecular models for the six membered δ-lactone. The occurrence of intermolecular reaction is supported by the formation of insoluble crosslinked products when the polymer was heated at 200° for 30 min.

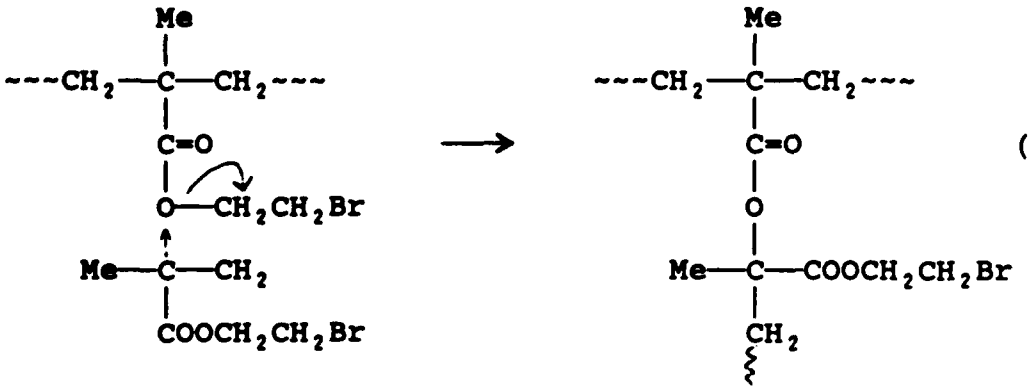
The pyrogram of PBEMA showed that ethylbromide is produced in

amounts greater than CH_3Br. Processes analogous to reactions 2 and 3 are suggested,



$$+ \cdot CH_2CH_2Br \quad (4)$$

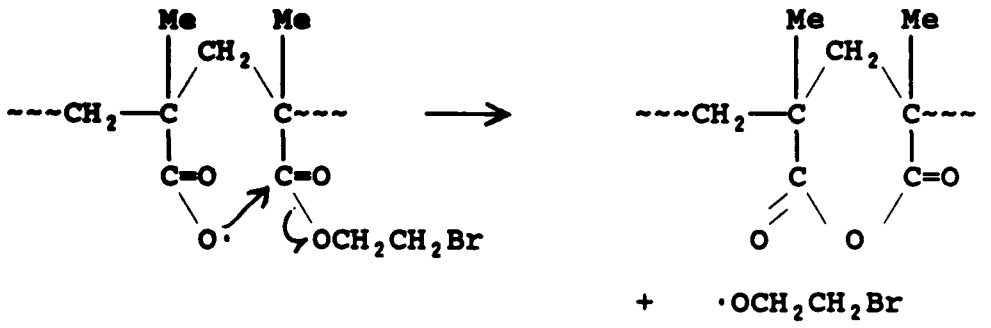
Intermolecular



(5)

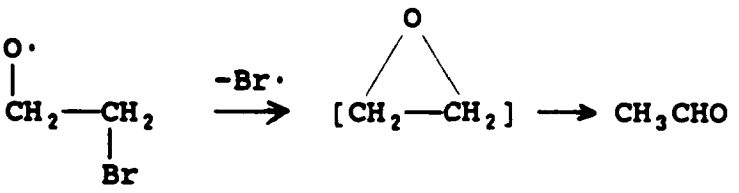
The intramolecular process is favoured here because of the formation of the stable γ-lactone. Of course ethyl bromide is formed from $BrCH_2CH_2\cdot$ radical by hydrogen abstraction.

Acetaldehyde is probably a product of bromoethoxy radical liberated by the following pathway,



(6)

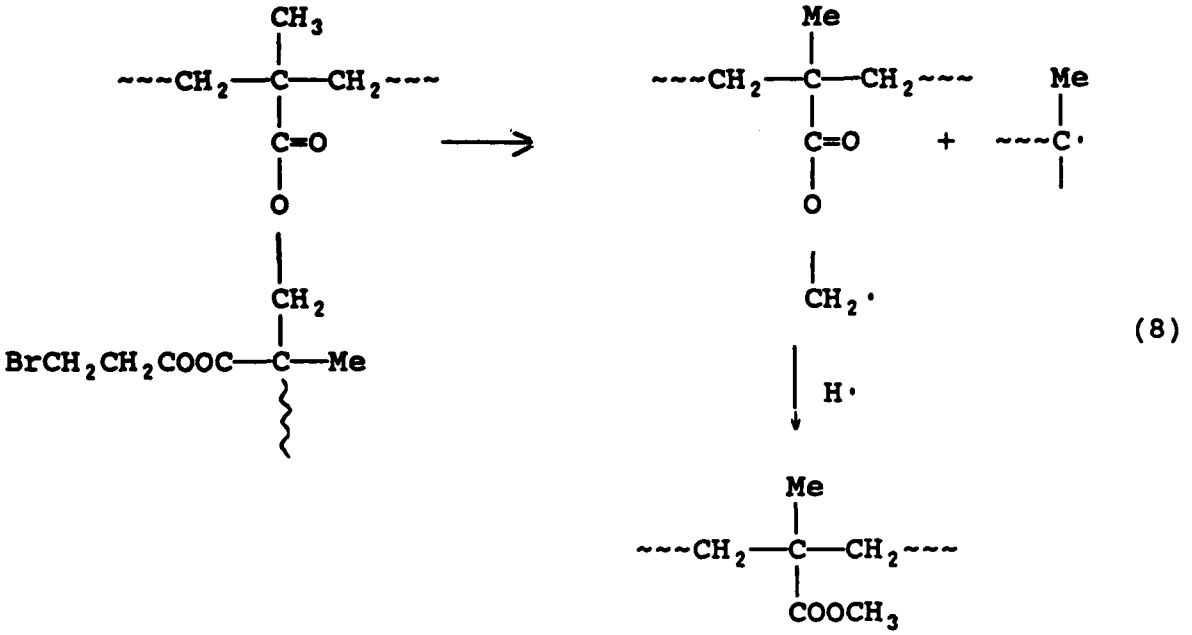
As described earlier[6] bromoethoxy radical loose bromine atom at elevated temperature to give ethylene oxide intermediate which rearranges to acetaldehyde.



(7)

The fact that no bromoethanol could be detected indicates that bromoethoxy radical preferentially cleaves the C-Br bond rather than abstraction of hydrogen. Grassie et al.[9] has also found that degradation of polyethylacrylate gave acetaldehyde as a major product over ethanol.

The production of a very small amount of MMA may be related to the crosslinked structures in eqs. 3 and 5. If there is scission of the C-C bond two radicals were generated, one of which abstracts a hydrogen atom to introduce MMA units in the chain as shown in equation 8.



(8)

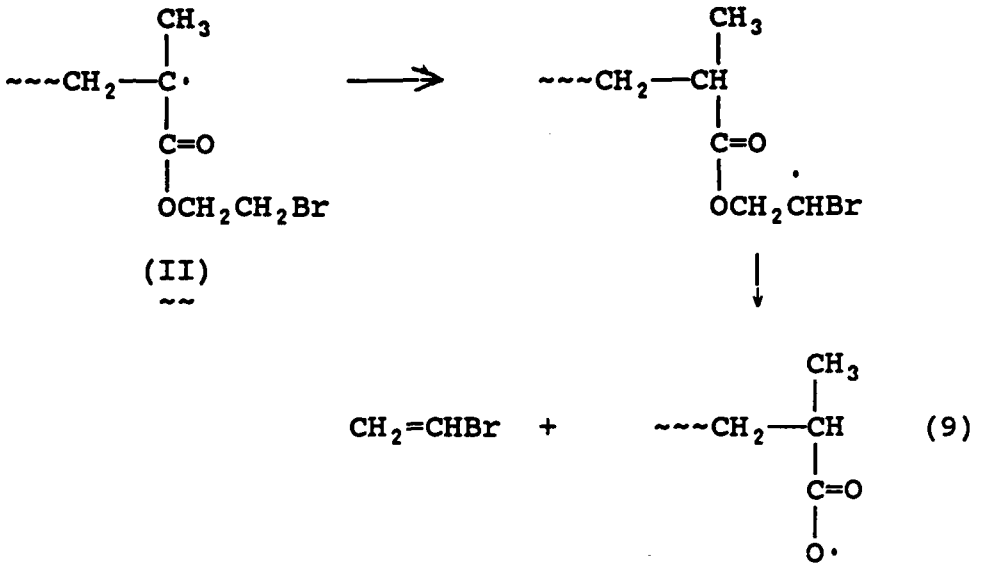
Subsequent pyrolysis should yield the observed MMA.

The similarity of products of pyrolysis of PBEMA and poly(2-fluoroethyl methacrylate) (PFEMA)[6] suggests a commonality in their mechanisms of degradation. Both polymers produce acetaldehyde, vinyl halide and carbon dioxide. Acetaldehyde is the reaction product of haloethoxy radical formed via intra/intermolecular reactions as discussed above. However, the fluoroethoxy radicals also forms fluoroacetaldehyde in addition to acetaldehyde, whereas the bromoethoxy radicals gave only acetaldehyde. This difference may be due to electronegativity and size effects of the halogen atoms on the haloethoxy radicals. It is surprising that none of the polymers produced halogenated alcohol.

Poly(78MMA-co-2,2-BEMA)

The pyrogram of the copolymer as illustrated in Figure 3 and the products of pyrolysis are given in Table III. The major products of pyrolysis are CO_2, CH_3Br, MMA; the minor products are vinyl bromide and acetaldehyde. The unexpected observation is that CH_3Br is formed in much larger proportion than vinyl bromide. This may be explained if degradation reactions 2 and 3 occur for a sequence of MMA units in the copolymer chain.

The initiation event is random scission of main chains which is followed by depropagation liberating MMA monomer units. The depropagation ceases when it reaches a BEMA unit in the copolymer. However, at other conditions, i.e., heating to 500° at 10°/min in N_2, depropagation can be the dominant degradation pathway for PBEMA, poly(MMA-co-BEMA) copolymers and PBEMA and polymethylacrylate blends, as found by Grassie et al.[7] In our case, radical II undergoes intramolecular H abstraction with a five membered ring transition state to yield vinyl bromide.

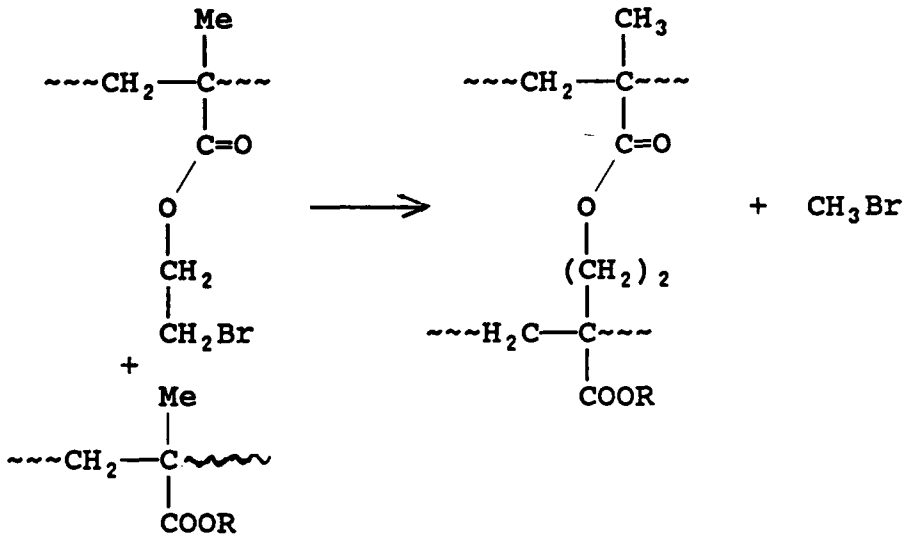


(II)

$$CH_2{=}CHBr + \sim\sim\sim CH_2{-}\underset{\displaystyle C{=}O \cdot}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}} \qquad (9)$$

The reactivity of the secondary hydrogen atoms toward abstraction may be enhanced by electron withdrawing the bromine substitution which decreases the strength of the C-H bond.

Comparison of pyrolysis and radiolysis data[3] clearly suggests that the mode of scission is entirely different in spite of the formation of a few common products by both processes. The principal product missing in the radiolysis studies on PBEMA and poly(BEMA-co-MMA) was ethylbromide. Formation of CH_3Br in the radiolysis of PBEMA was shown to occur by an alternative route[3] as shown in equation 10,



(10)

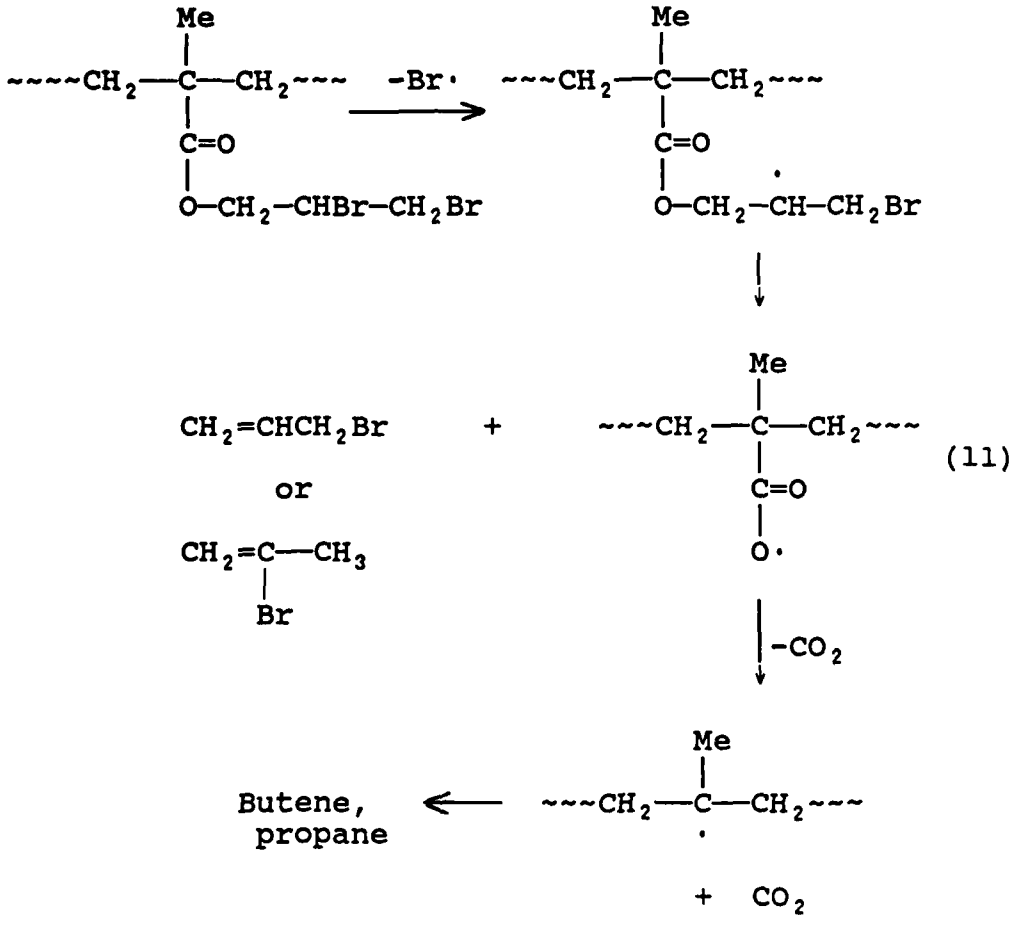
The ease of crosslinking was explained on the basis that the heavy bromine atom has low diffusabitily at room temperature.

Poly(2,3-dibromopropylmethacrylate) (PDBPMA)

Thermogravimetric analysis of PDBPMA showed a single stage weight loss till 380° with about 78% weight loss. The course of degradation beyond 380° is changed slightly toward complete degradation. The pyrogram of PDBPMA is shown in Figure 4 and the products are listed in Table IV. The principal products include CO_2, acetaldehyde, CH_3Br, and isomers of alkyl bromide. Traces of ethyl bromide was also detected. The mechanism of degradation is governed mainly by ester decomposition.

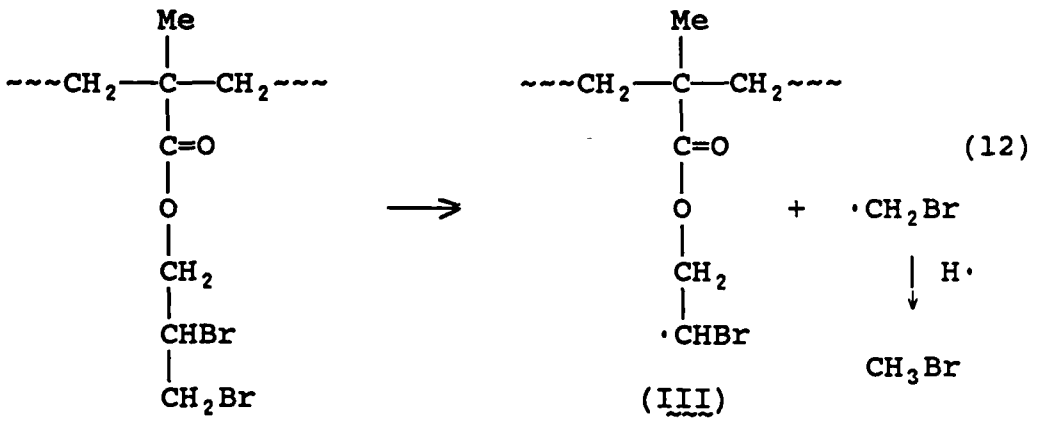
The tertiary C-Br bond is the most vulnerable one to thermolysis, followed by the ester C-O bond. The end result is the formation of isomers of alkyl bromide (assignments of the

relative peaks of isomeric products needs calibration with authentic samples). Formation of various products may be shown in a sequence of degradation steps (eq. 11).



(11)

The production of CH_3Br suggests the cleavage of C-C facilitated by steric effects of the two bromine atoms followed by abstraction of hydrogen atom,

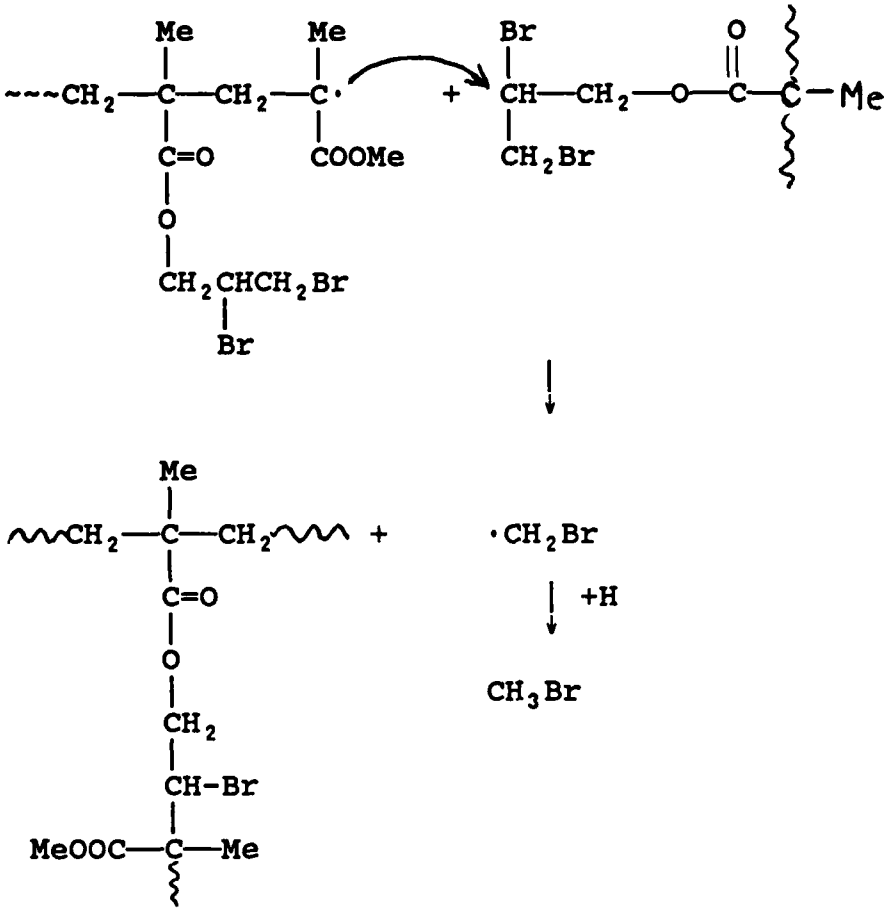


(12)

The other products may follow the same degradation process as described under PBEMA.

Poly(84 MMA-co-16 DBPMA)

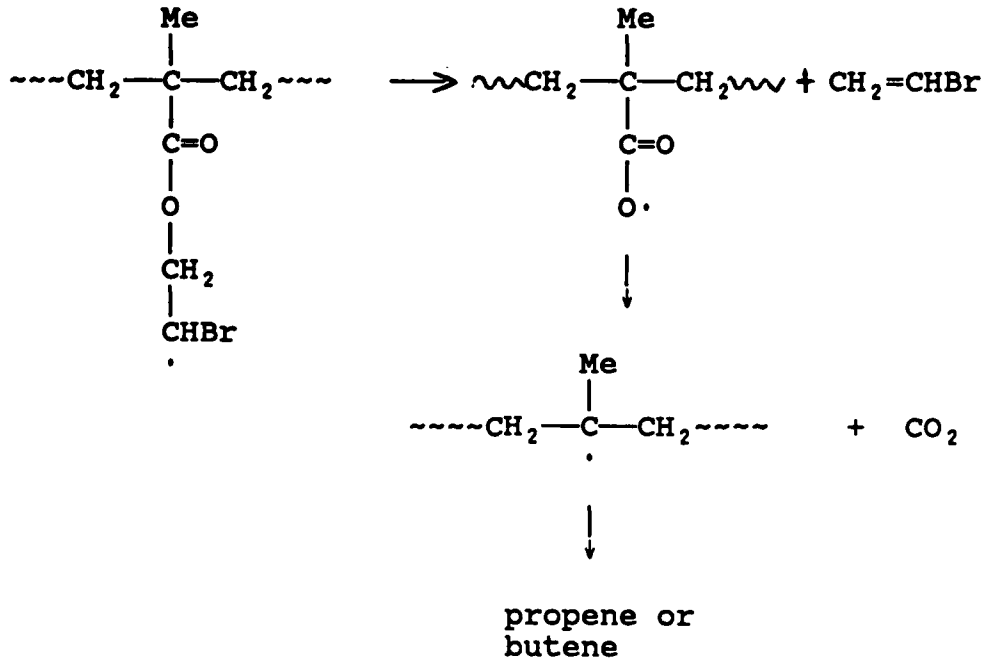
The pyrogram is shown in Figure 5, and the products are given in Table V. The important departures noted in this pyrogram of the copolymer as compared to PDBPMA are: (i) concentration of CH_3Br is higher, (ii) additional products include vinyl bromide and MMA monomer. Since the copolymer is rich in MMA units, initial stages of degradation is always accompanied by main chain rupture in the polymer containing MMA sequences followed by depropagation to MMA monomer. These propagating chains undergo intermolecular reactions with ester chains liberating $\cdot CH_2Br$ radicals.



(13)

The intermolecular reactions will lead to crosslinked polymers.

The radical III (of eq. 12) may rearrange to produce vinyl bromide and CO_2,



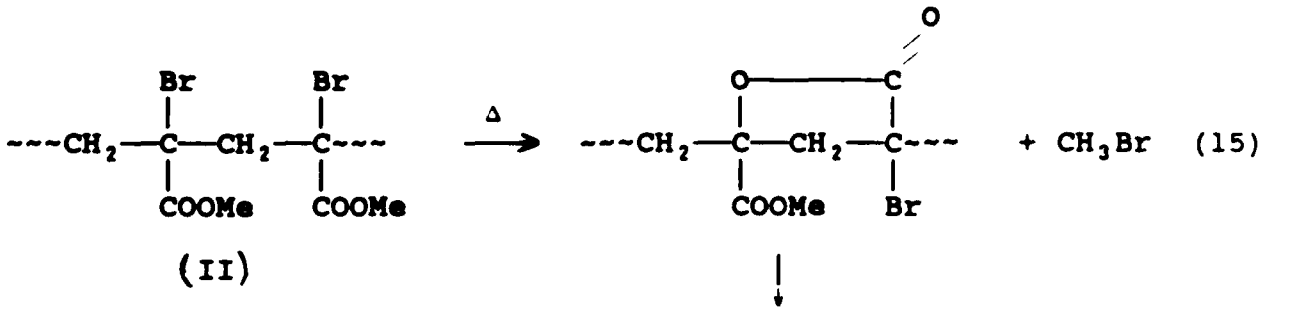
(14)

Comparison of radiolysis[2] and thermolysis of PBEMA and its copolymer revealed some interesting differences. The absence of vinyl bromide among the radiolysis products shows that the reaction does not involve six membered transition state as postulated for thermal degradation. The presence of brominated products in radiolysis suggests alternate mechanism of degradation, viz, through random scission. The fundamental difference in the mode of degradation between the two processes might be attributed to the temperature at which the degradation was carried out. Radiolysis of polymers was performed at room temperature i.e., below T_g of homo and copolymers. The reduced thermal motion of ester side chains below T_g tends to retard the formation of the cyclic intermediates in eqs. 2 and 4 for

degradation. However, random scission of main chains with the consequent liberation of vinyl bromide as shown in eqn. 9 is feasible at the high temperature for thermal degradation. Furthermore, the formation of higher concentration of vinyl bromide in thermolysis would yield reactive carboxylate radical which can participate in intramolecular reactions producing anhydride structures (eq. 6). It is reasonable to expect that the anhydride units would inhibit depolymerization. However, there is no data on the radiolysis of PDBPMA for comparison with the thermal decomposition results.

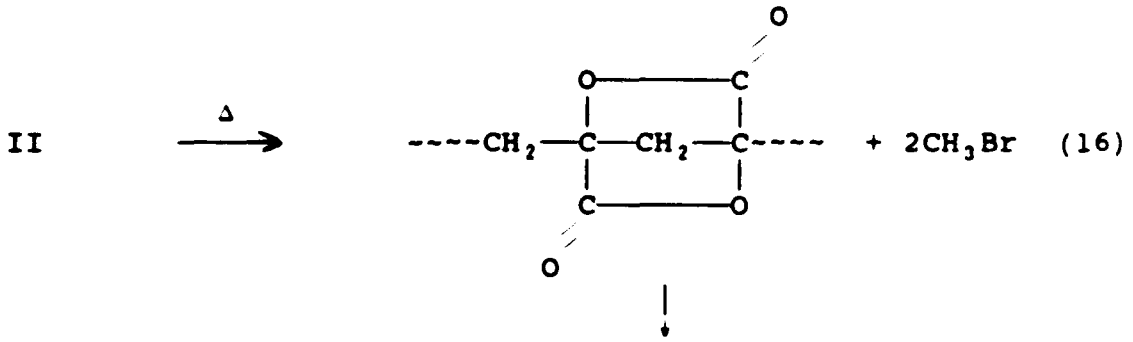
Poly(methyl-α-bromoacrylate) (PMBA) and poly(MMA-co-22MBA)

The TGA curve of PMBA showed two distinct stages of weight loss (Figure 1). The weight loss during the first stage is 56% which corresponds exactly to the weight fraction of CH_3Br in PMBA. The residue at the first plateau may be free of any bromine. One or more mechanisms are possible. Elimination of CH_3Br can occur intra or intermolecularly. If intramolecular elimination occurs one would expect mono and/or dilactone structures



(II)

alkenyl bromide products



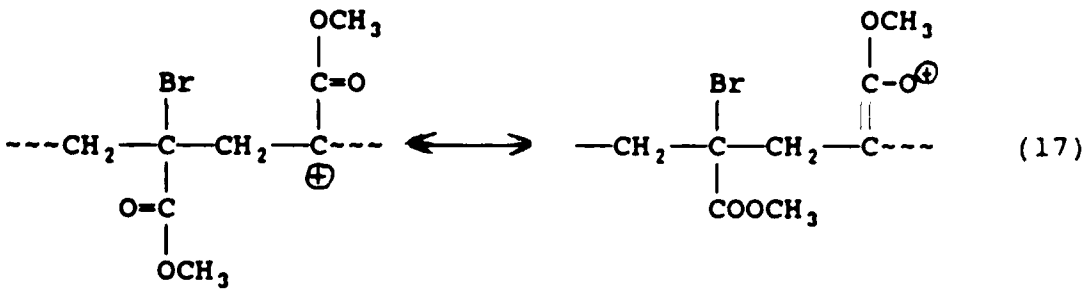
CO_2, butene, propene

Intermolecular elimination of CH_3Br should yield a crosslinked product. The solubility characteristics and isothermal studies on PMBA suggests intramolecular reactions. This is suggested by a pronounced increase in 1790 cm^{-1} band with time of isothermal heating of PMBA which has been attributed to lactone formation.

The pyrograms of PMBA and poly(78 MMA-co-22MBA) are illustrated in Figures 6 and 7 and their degradation products are listed in Tables VI and VII. The principal pyrolysis products of PMBA are CH_3Br and CO_2. This supports the above interpretation of the thermogravimetric data. The pyrolysates of copolymer are

CH_3Br, MMA and some other unidentified products.

Methyl bromide elimination can be envisioned to occur by one of three different pathways: an S_N1 type reaction, an S_N2 type reaction, and concerted addition. The S_N1 mechanism involving the formation of a tertiary carbonium ion is unfavourable because of the strong electron withdrawing effects of the carbonyl group. Once formed, the cation would be destabilized by the ester group, since delocalization of electrons would result in a resonance structure containing a positive, single bonded oxygen.

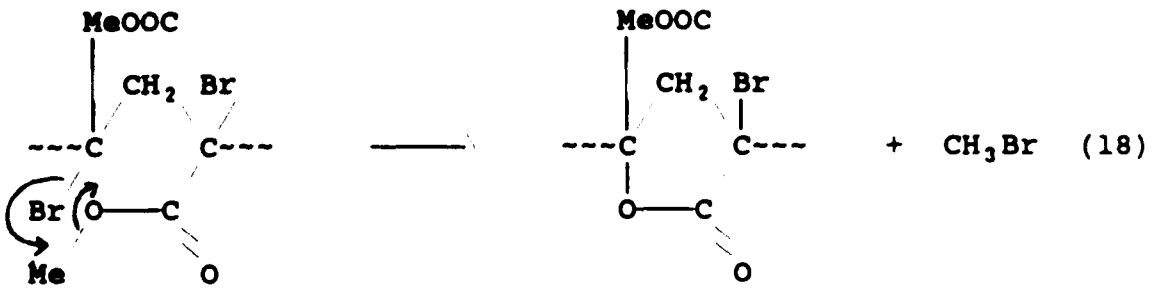


(17)

On the other hand, a carbon atom located adjacent to both a bromine and a carbonyl function could have enhanced reactivity towards S_N2 nucleophilic attack. But it is doubtful that the ester oxygen is not sufficiently basic to function as a suitable nucleophile. Moreover, this type of reaction is usually very sensitive to steric effects, the reactivity can be significantly lowered by bulky groups.

The third pathway involving concerted addition emerges as the most probable of the three. The following molecular

representation depicts a possible model for the transition state which leads to the production of a γ-lactone ring.



This proposed mechanism is also consistent with previous lactonization studies on poly(α-bromoacrylic acid).[10]

ACKNOWLEDGEMENT

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Figure Captions

Figure 1 TGA of (---) PBEMA (——) PMBA and (-·-) PDBPMA.

Figure 2 Pyrogram of poly(2-bromoethyl methacrylate).

Figure 3 Pyrogram of poly(78 MMA-co-22 BEMA).

Figure 4 Pyrogram of poly(2,3-dibromopropyl methacrylate).

Figure 5 Pyrogram of poly(84 MMA-co-16 DBPMA).

Figure 6 Pyrogram of poly(methyl-α-bromoacrylate).

Figure 7 Pyrogram of poly(78 MMA-co-22 MBA).

Table I. TGA of Bromine Containing Poly(acrylates)

Polymer	Degradation Temperature at Various wt. Cases				T_{max}
	10%	30%	50%	70%	°C
PMBA	155	170	225	370	206
PBEMA	245	365	387	410	319
PDBPMA	275	315	327	350	291

Table II. Pyrolysis Products of Poly(2 BEMA)

Peak	Identification
1	CO
2	CO_2
3	Propene
4	Acetaldehyde
5	$CH_3{}^{79}Br$ $CH_3{}^{81}Br$
6	butene
7	vinyl bromide
8	ethyl bromide
9	MMA

Table III. Pyrolysis of Products of Poly(78 MMA-co-22 BEMA)

Peak	Identification
1	CO_2
2	Propene
3	CH_3CHO
4	CH_3Br
5	Butene
6	CH_2=CHBr
7	unidentified
8	MMA

Table IV. Pyrolysis Products of Poly(DBPMA)

Peak	Identification
1	CO_2
2	Propene
3	Acetaldehyde
4	$CH_3{}^{79}Br$, $CH_3{}^{81}Br$
5	Butene
6	C_2H_5Br
7	Alkylbromide
8	Bromocyclopropane (or) 2 bromopropane

Table V. Pyrolysis of Poly(84 MMA-co-16-DBPMA)

Peak	Identification
1	CO
2	CO_2
3	$CH_2=CH_2$
4	Propene
5	CH_3Br
6	Butene
7	$CH_2=CHBr$
8	C_2H_5Br
9	Alkyl bromide
10	$CH_3CH=CHBr$
11	$CH_3C-Br=CH_2$
12	Cyclopropyl bromide
13	MMA

Table VI. Pyrolysis Products of PolyMBA

Peak	Identification
1	CO_2
2	Propene
3	Methyl bromide
4	Vinyl bromide

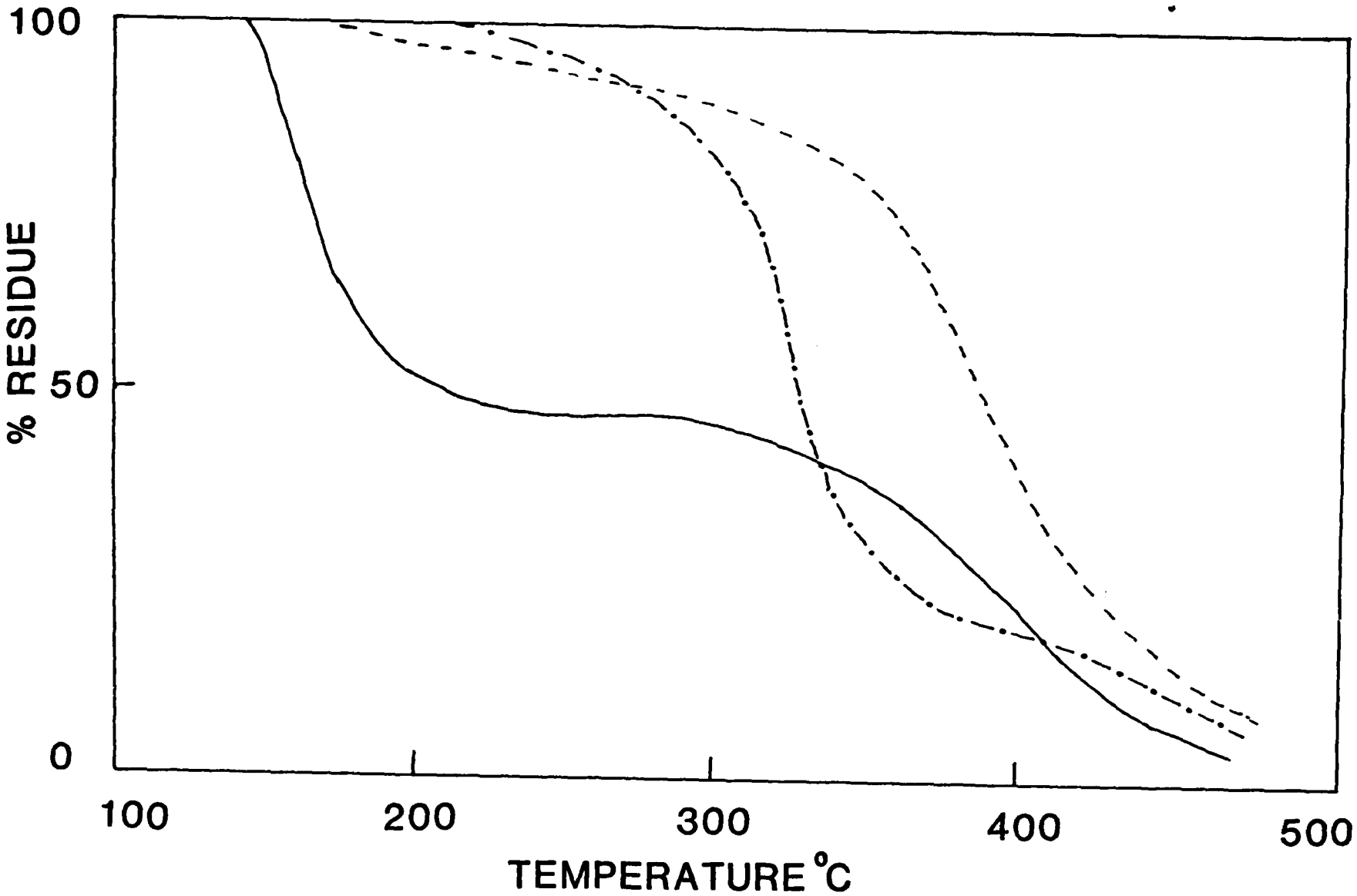

FIG. 1.

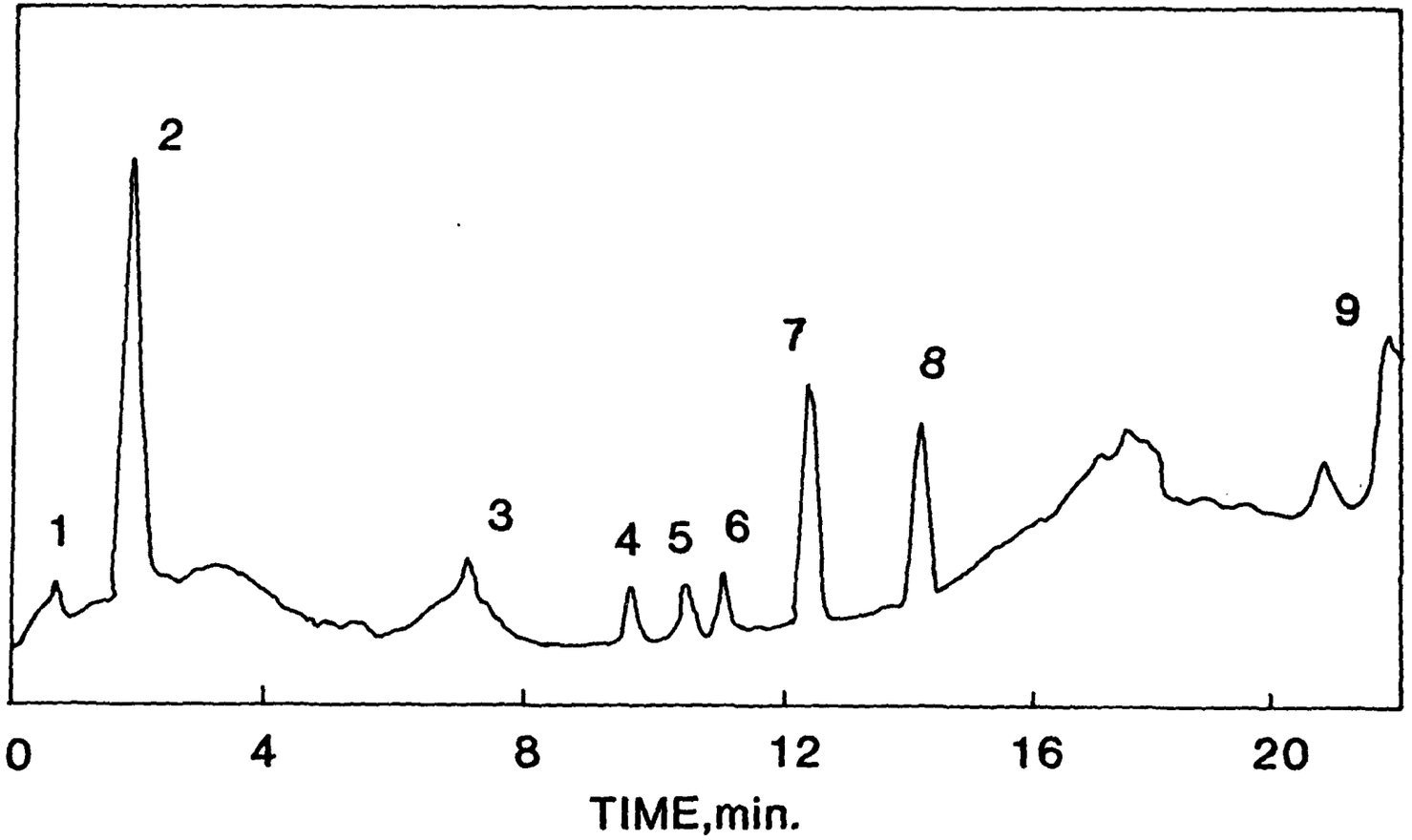

FIG.2.

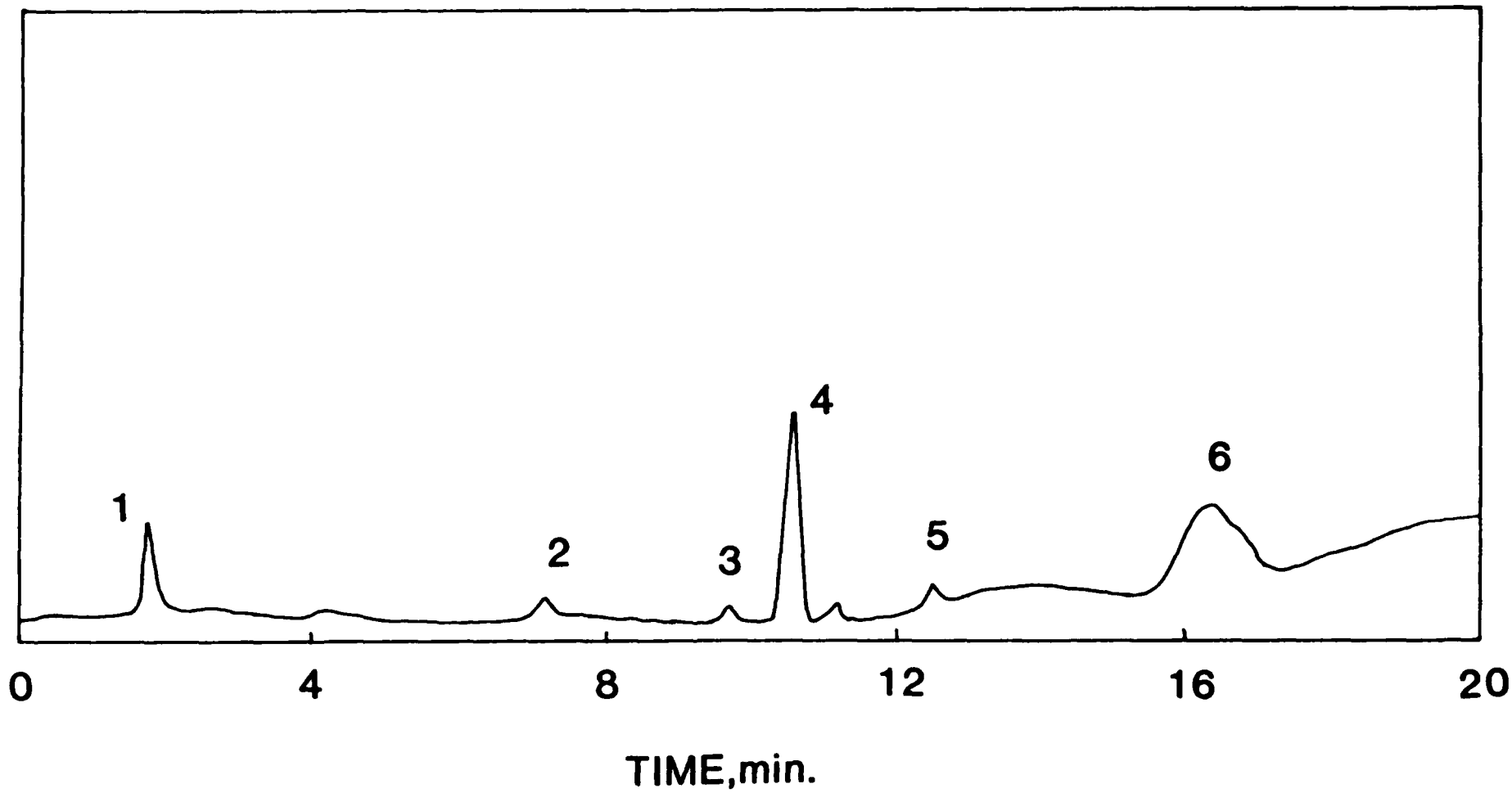

FIG.3.

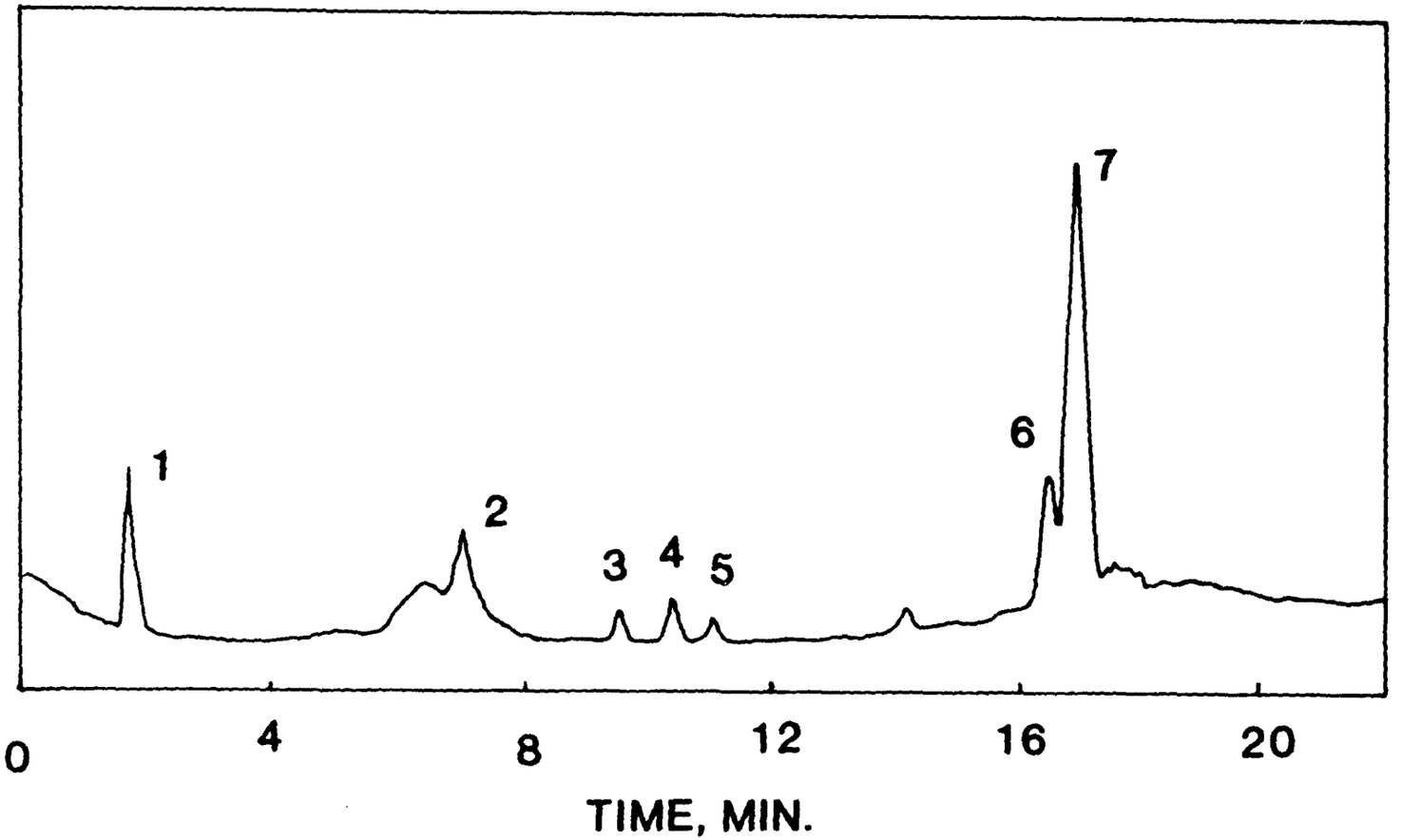

FIG.4.

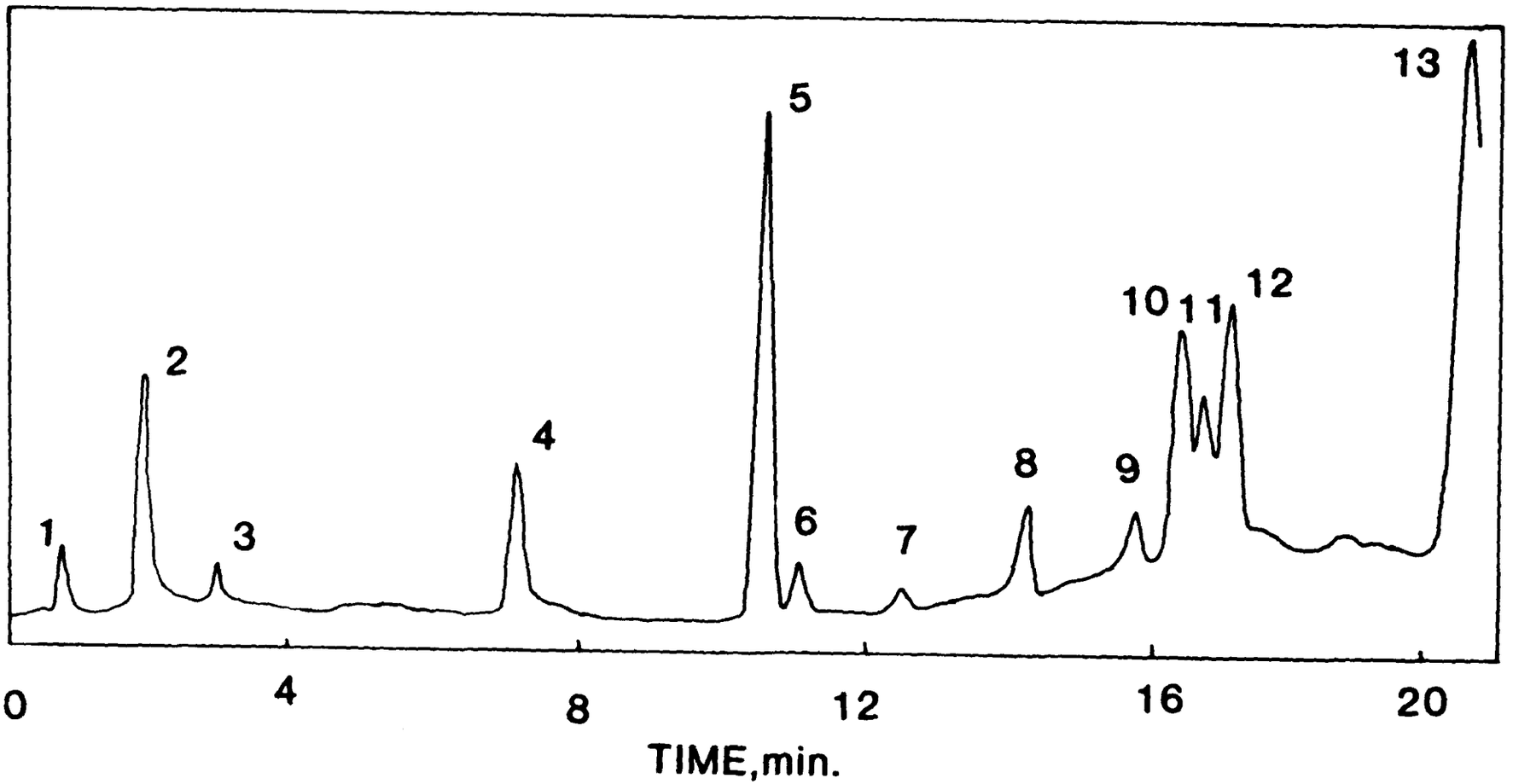

FIG.5.

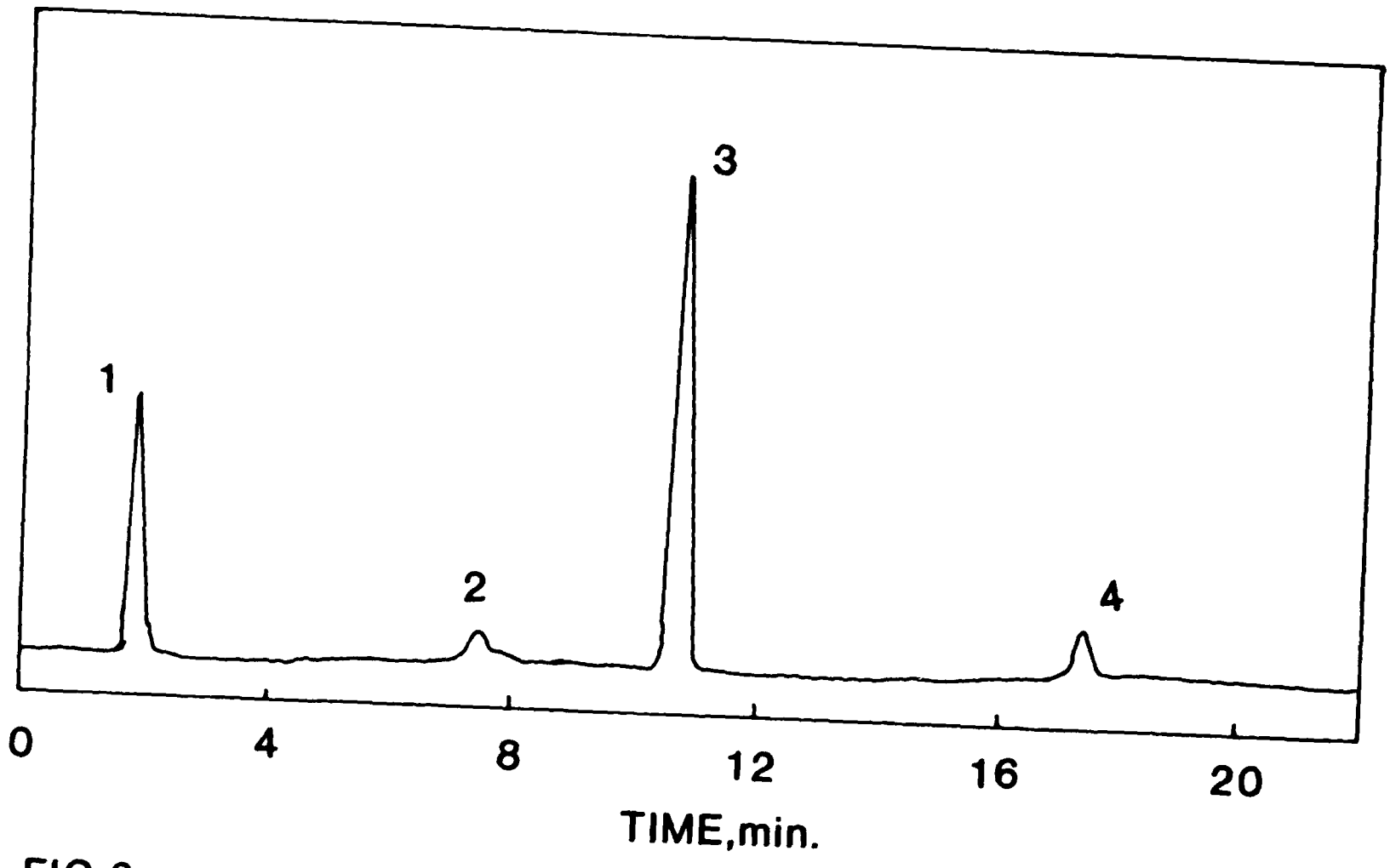

FIG.6.

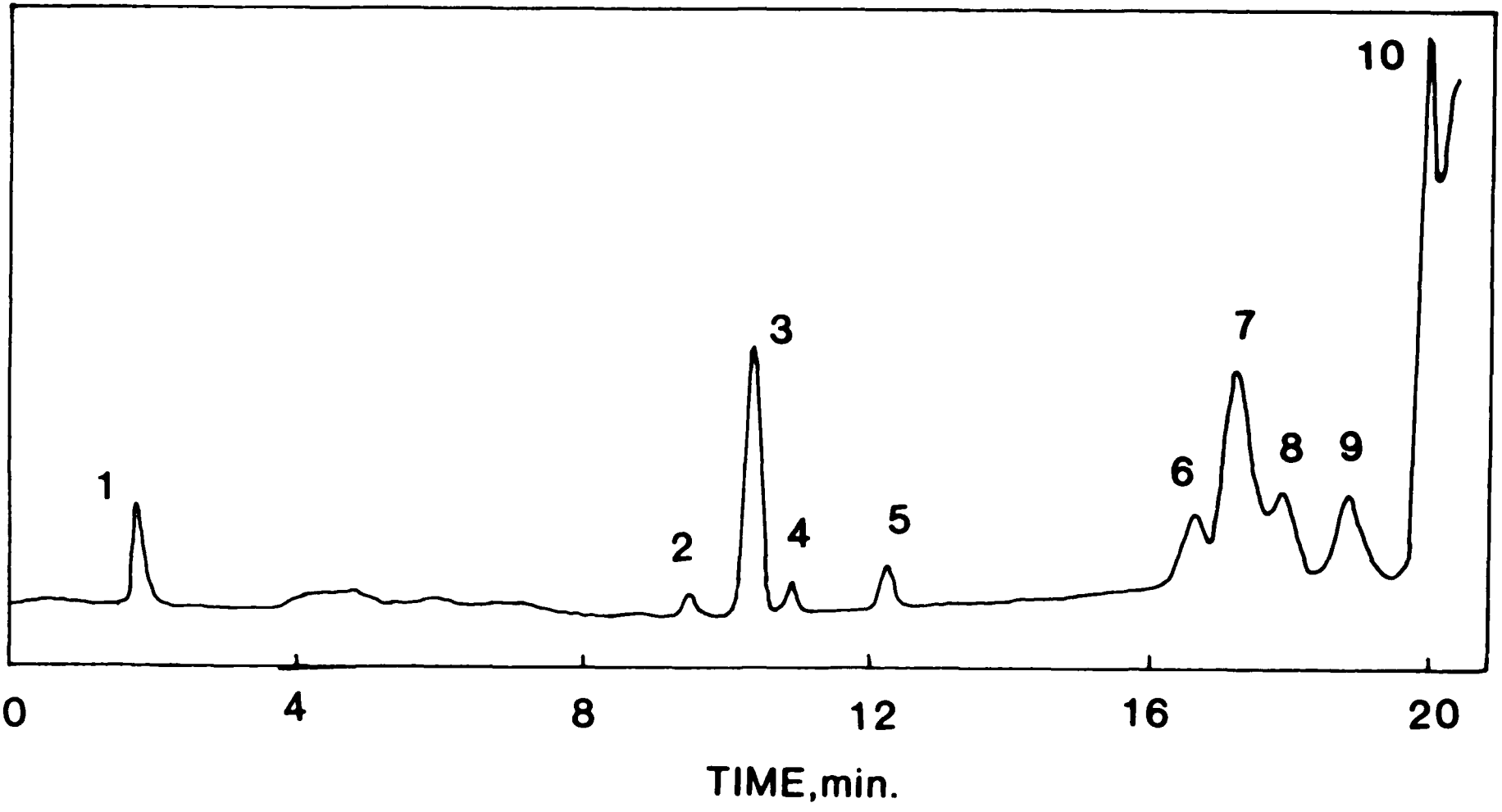

FIG.7.

END

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