Preparation and Characterization of Head-to-Head Polymers. II. Head-to-Head Poly(methyl Acrylate)

T. Tanaka[a]; O. Vogl[a]

[a] Polymer Science and Engineering University of Massachusetts, Amherst, Massachusetts

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T. TANAKA and O. VOGL

Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01002

ABSTRACT

Head-to-head poly(methyl acrylate) was prepared by ester-
ification of the known alternating copolymer of ethylene and
maleic anhydride. Some of the chemical, physical, and
mechanical properties and the thermal degradation behavior
of head-to-head poly(methyl acrylate) were studied and
compared with those of head-to-tail poly(methyl acrylate).
The T_g of the head-to-head polymer was higher than that of
the head-to-tail polymer, but the solubilities of both types
of polymers of comparable molecular weight were similar.
Head-to-head poly(methyl acrylate) degraded thermally at
approximately the same temperature and with a rate
similar to head-to-tail poly(methyl acrylate). Unlike
poly(methyl cinnamates) which cleanly degraded to
monomers, poly(methyl acrylates), head-to-head and head-
to-tail, degrade to very small molecules, such as CO_2,
methanol, but also larger polymer fragments and char. Trace
amounts of monomers (methyl acrylate) were also observed.

INTRODUCTION

In our continuing work on head-to-head (H-H) polymers [1], we prepared and characterized H-H poly(methyl acrylate) and compared it with head-to-tail (H-T) poly(methyl acrylate).

We had earlier found that H-H poly(methyl cinnamate) is substantially different from the H-T polymer in solubility and degradation behavior but that the degradation products of both polymers are very similar.

Poly(methyl acrylate) was readily accessible from the well-known ethylene maleic anhydride alternating copolymer [2, 3]. Alternating ethylene/maleic anhydride copolymer as an intermediate has been used previously for various polymer reactions but the preparation of the dimethyl ester, poly(methyl acrylate), was only recently accomplished by Otsu [5]. In his paper the preparation of the ester was reported and the polymer briefly characterized.

In our study H-H poly(methyl acrylate) was prepared from alternating ethylene/maleic anhydride copolymer and the polymer was characterized extensively.

EXPERIMENTAL PART

Materials

Ethylene was obtained from Matheson Gas Products and used without purification. All the chemicals except benzoyl peroxide (BPO) were obtained from the Eastman Kodak Chemical Co.

Maleic anhydride (10 g) was dissolved in dry benzene (100 ml) and pressure filtered. The solution was used directly for polymerization. Eastman's maleic anhydride contained a few percent of insoluble material, presumably maleic acid, which had to be removed prior to the use of maleic anhydride as monomer for polymerizations.

Azobisisobutyronitrile (AIBN) was purified by recrystallization three times from dry methanol and was dried overnight at room temperature at 0.1 Torr.

Benzene was used from freshly opened bottles and used without purification.

BPO was recrystallized three times from dry ethanol before use and dried at 0.1 Torr overnight at room temperature.

Methyl acrylate was dried over sodium sulfate for several hours and then distilled under reduced pressure and under nitrogen before use. The monomer contained less than 0.5% of impurities according to gas chromatography.

Copolymerization of Ethylene and Maleic Anhydride

Although ethylene/maleic anhydride alternating copolymer was at one time available from GAF [2], we prepared our own copolymer according to the preparation in Macromolecular Syntheses [3]. This synthesis describes yields of copolymer in the 90% range as compared to maleic anhydride. It was more common under our experimental conditions to obtain 50 to 60% yields of copolymer. The only difference between our work and the preparation in Ref. 3 was that we used regular ethylene and we were informed that they used polymerization-grade ethylene to carry out the copolymerization.

We used a 1-liter rocking autoclave with a glass sleeve. The autoclave was commonly filled to 300 ml capacity at an ethylene pressure of 30 atm; BPO was used as the initiator. The copolymer precipitated during the reaction and was obtained in a highly swollen form. Dichloromethane was added at the end of the reaction to precipitate the polymer completely; the polymer was then washed and finally dried under reduced pressure.

Esterification of Alternating Ethylene/Maleic Anhydride Copolymer

Alternating ethylene/maleic anhydride copolymer was esterified with methanol and sulfuric acid according to Fisher's method [4]. This method gave a very incomplete esterification, the polymeric anhydride reacted to form essentially only the polymeric half ester. In order to prepare completely esterified polymers, the initially prepared polymer must be isolated and further esterified by reacting it with diazomethane [6].

Polymerization of Methyl Acrylate

Methyl acrylate was polymerized by conventional radical polymerization using AIBN as the initiator [7].

Measurements

A Perkin-Elmer DSC-1B differential scanning calorimeter was used for the determination of the thermal behavior of the polymers, including the determination of the glass transition temperature (T_g).
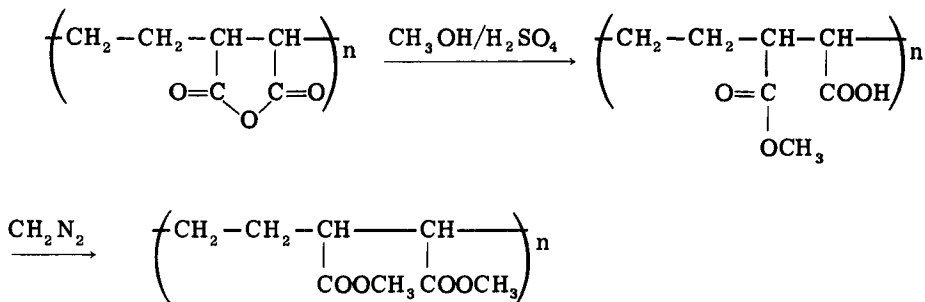
The thermal degradation studies of all polymers (DGA) were carried out in a nitrogen atmosphere using a Perkin-Elmer TGS-1 thermal balance. Most thermal degradation results of these polymers are reported as DTG (differential thermal gravimetric analysis) at a programmed temperature increase of 5°C/min [8].

The NMR studies were carried out with a Hitachi Perkin-Elmer R-24 instrument.

The polymers were also analyzed by pyrolysis gas chromatography. A Hewlett Packard Model 80 pyrolyzer was used for the analysis of the samples. The polymer samples were held in a Pt-Rh electrode and the desired pyrolysis temperature was obtained by applying the appropriate voltage; the electrode was heated for about 10 sec for a sample size of about 1 mg. The pyrolysis products were directly passed with a carrier gas (helium) into a Varian Aerograph Model 920 and analyzed on a column of SE-30 (silicon gum rubber) or diisodecylphthalate. The column was 6 ft long and of 1/8 in. diameter; the column temperature was 85°.

RESULTS AND DISCUSSION

Alternating ethylene/maleic anhydride copolymer was readily prepared according to previous reports [2, 3]. This copolymer could be transformed into the acid ester by allowing the polymer to react with methanol in the presence of sulfuric acid. The simple technique of opening the cyclic anhydride to form the half ester worked well in this case but was not usable in the case of our alternating stilbene/maleic anhydride copolymer reported earlier [1] because this polymer was not soluble and not wettable.

$$\left(CH_2-CH_2-CH-CH\right)_n \xrightarrow{CH_3OH/H_2SO_4} \left(CH_2-CH_2-CH-CH\right)_n$$

$$\xrightarrow{CH_2N_2} \left(CH_2-CH_2-CH-CH\right)_n$$

Further esterification of the polymeric half ester derived from alternating ethylene/maleic anhydride copolymer under more rigorous esterification conditions was not successful. However, the polymer could be isolated and further treated with diazomethane to completely esterify this polymer to H-H poly(methyl acrylate).

Figure 1 shows the IR spectra of the original alternating ethylene maleic anhydride copolymer, the ester acid, and the completely esterified H-H poly(methyl acrylate). The alternating ethylene maleic anhydride copolymer (Fig. 1a), shows that the functional groups of the
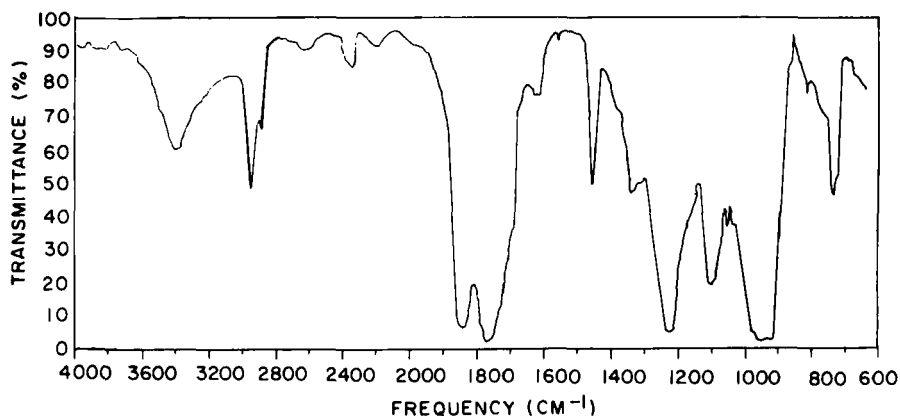
FIG. 1a. IR spectrum of ethylene maleic anhydride alternating copolymer.
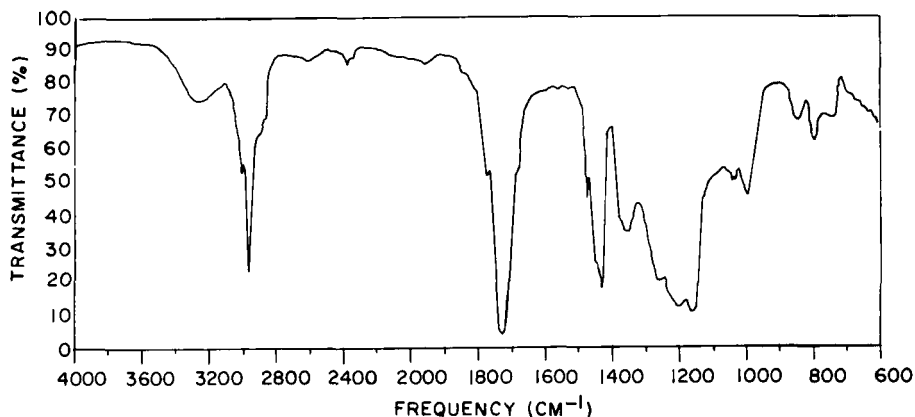
FIG. 1b. IR spectrum of half ester of ethylene maleic anhydride alternating copolymer.

polymers are in the cyclic anhydride form, similar to a substituted succinic anhydride as expected from the copolymerization, although a trace amount of acid is noticeable. There are strong ester bands in the half ester form (Fig. 1b) of the polymer at 1725 cm^{-1}, but free acid bands can also be clearly distinguished. From the intensity

FIG. 1c.   IR spectrum of H-H poly(methyl acrylate).

of these bands it can be estimated that the amount of acid and ester function is about equal in the polymer. In the wholly esterified form (Fig. 1c), the H-H poly(methyl acrylate), there are no anhydride groups and no free acid groups, but only ester groups.
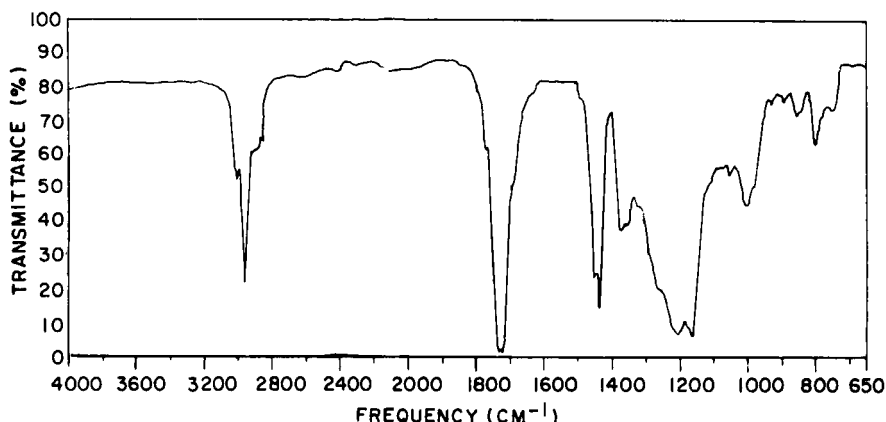
IR techniques for free acid groups probably have a confidence limit of only approximately 3 mole % of carboxylic acid group. Consequently, the absence of a group in the IR spectrum only means that, as far as the IR technique is concerned, less than the indicated amount is present.

Table 1 shows a comparison of the specific viscosity of the initial polymers and the esterified polymers. The polymer shows an adequately high solution viscosity and consequently molecular weight for physical measurement. Some molecular weight loss occurred during the esterification of the polyanhydride. It could have been caused by breakage of interchain polyanhydride linkages during the esterification.

Elemental analysis also indicated that a completely esterified H-H poly(methyl acrylate) was obtained by this esterification technique.

In addition to H-H poly(methyl acrylate), H-T poly(methyl acrylate) was prepared by conventional free radical polymerization of methyl acrylate [7]. The IR spectrum (Fig. 2) of H-T poly(methyl acrylate) was compared to the H-H polymer. Although many similarities exist between those two polymers, substantial differences can be noticed, particularly in the fingerprint region between 1000 and 600 cm^{-1}.

We have done initial work on the NMR spectrum of H-H poly(methyl acrylate) and H-T poly(methyl acrylate). This work

TABLE 1. Copolymerization of Ethylene and Maleic Anhydride and Analysis of H-H Poly(methyl acrylate)[a]

Copolymerization								Analysis of H-H poly(methyl acrylate)		
Initiator amount		Polymerization temperature (°C)	Polymerization time (hr)	Polymer yield		η_{sp}/c[b]	η_{sp}/c[b]	Elemental analysis (%)		
gram	mmole			grams	% of MAn charged			C	H	O
0.532	2.2	70	20	17.6	45	0.40	-	-	-	-
0.048	0.2	60	42	11.8	30	1.02	0.77	56.0	7.10	37.0
0.048	0.2	60	45	11.8	30	1.13	0.80	56.6	7.11	36.8
							Theory:	55.8	7.03	37.2

[a]Copolymerization conditions: solvent, 300 ml benzene; initiator, benzoyl peroxide; comonomers: maleic anhydride (MAn), 39.2 g (400 mmole); ethylene pressure, 30 atm.
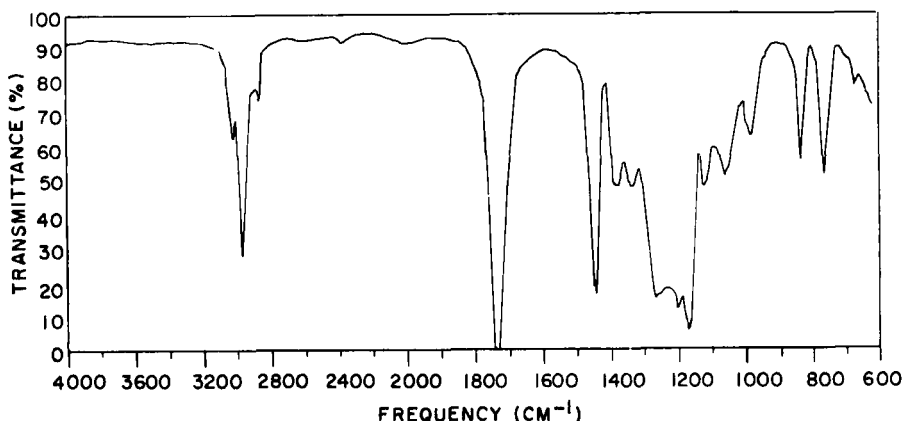[b]0.2 g/dl in dimethylformamide at 30°C.

FIG. 2. IR spectrum of H-T poly(methyl acrylate).

was done in deutero-chloroform as solvent at room temperature with a 60 MHz NMR spectrometer, and the study is only qualitative because it was carried out at room temperature where there is not enough resolution to draw any conclusions about the stereochemistry of the polymers.

H-H poly(methyl acrylate) has three major regions of resonance at a ratio of 4:2:6.

The four methylene protons have a chemical shift peaking around 1.4 ppm, the methin protons at 2.6 ppm, and the methoxy protons at 3.6 ppm.

In the case of H-T poly(methyl acrylate), the methylene protons are at 1.8 ppm, the methin protons at 2.3 ppm, and the methoxy protons at 3.5 ppm., again in a ratio of 4:2:6.

More extensive work on the stereochemistry of these polymers is planned with the aid of a higher resolution NMR spectrometer at higher temperatures.

The thermal behavior of H-H poly(methyl acrylate) and H-T poly(methyl acrylate) was studied by differential scanning calorimetry (DSC) at a heating rate of 5°C/min under nitrogen. Glass transition temperatures (T_g) of the polymers were determined for H-H poly(methyl acrylate) as 31°C and for H-T poly(methyl acrylate) 7°C. These values agree well with previously determined values [4, 8].

Surprisingly, thermal gravimetric analysis of H-H poly(methyl acrylate) and H-T poly(methyl acrylate) showed that the degradation temperature and the maximum rate of degradation of both polymers were essentially the same (Fig. 3). The initial degradation temperature for the H-H polymer was extrapolated to 368°C and for the H-T
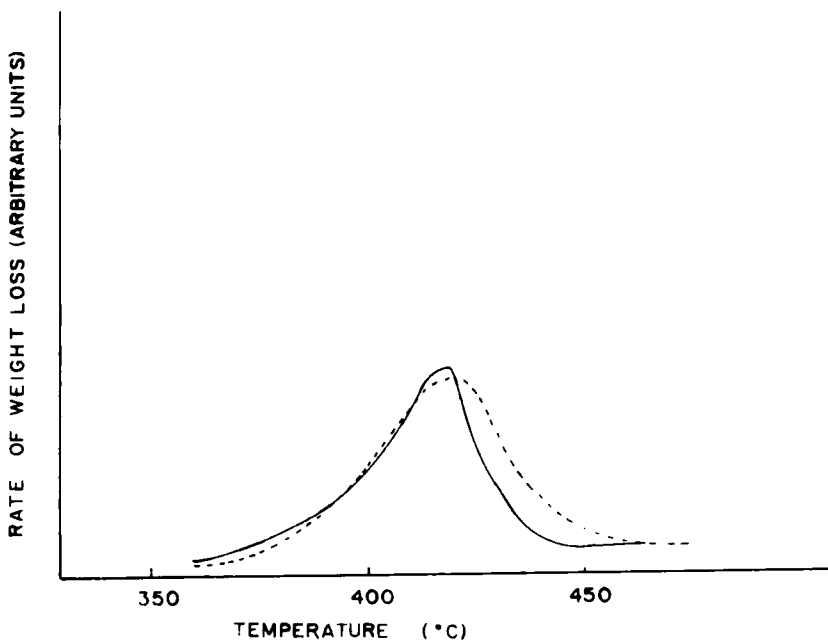
FIG. 3. Thermogravimetric spectra of H-H and H-T poly(methyl acrylate). Heating rate: 5°C/min.

polymers to 372°C while the maximum rate of degradation was at 418°C for the H-H polymer and 419°C for the H-T polymer. This great similarity appears surprising when one compares this data of the poly(methyl acrylates) with the data for H-H and H-T poly(methyl cinnamate). However, they are not surprising in view of Grassie's [11] earlier work on the thermal degradation of polystyrene where he suggested that the breakage of the H-T linkage in polystyrene does not require more energy than that of the H-H linkage.

Based on our experimental results, we can qualify this statement somewhat and amplify it. In our cases of substituted H-H and H-T poly(methyl acrylates), the degradation appears to commence at the same temperature and maximum rate using a programmed heating rate of 5°/min as long as there is no substitution on other parts of the molecules. If the methylene groups are substituted as in the case of poly(methyl cinnamate), where one of the hydrogens of the methylene groups is substituted by a phenyl group, the H-H polymer degrades at much lower temperature than the H-T polymer and the maximum rate of degradation also occurs at a much lower temperature.

H-H Poly(methyl acrylate) and H-T poly(methyl acrylate) were pyrolyzed near the temperature of maximum rate of degradation which had been determined beforehand by DTG and was found to be approximately 420°C. Pyrolysis products of poly(methyl acrylates) were totally different in kind from those observed in our earlier studies on the pyrolysis of H-H and H-T poly(methyl cinnamates).

As seen in Table 2, the major pyrolysis products were poly(methyl

TABLE 2. Relative Molar Ratios of Pyrolysis Products of Polymethyl acrylate[a]

Polymer	CO_2	MeOH	Acetone	MA	MMA	MVA	MCR
H-H	~8	4	0.2	1	-	0.5	0.2
H-T	~6	2.8	0.1	4	0.4	-	-

[a]MA: CH_2=CH—$COOCH_3$. MMA: CH_2=C(CH_3)—$COOCH_3$. MVA: CH_2=CH—CH_2—$COOCH_3$. MCR: CH_3—CH=CH—$COOCH_3$. H-H: head-to-head. H-T: head-to-tail.

acrylates), CO_2, and methanol. They constitute about 85% of the low-molecular-weight pyrolysis product in the case of H-H poly(methyl acrylate) and about 60% of the low-molecular-weight products of the H-T poly(methyl acrylate). As a consequence, a considerable amount of higher molecular weight fragments was obtained and more than 50% of the polymer was char in the case of both H-H or H-T polymers.

H-H Poly(methyl acrylate) and H-T poly(methyl acrylate) gave small amounts of the monomer methyl acrylate on pyrolysis. The relative amount was smaller in the case of H-H poly(methyl acrylate) and was the predominant compound of the pyrolysis products of the C3 and C4 fraction. In addition to methyl acrylate, in this fraction methyl vinyl acetate, methyl crotonate and acetone were present. In the case of H-H poly(methyl acrylate), methyl methacrylate was absent.

In the case of H-T methyl acrylate, the methyl acrylate portion of the C3 and C4 portion was significantly higher than in the case of the H-H polymer. A substantial amount of methyl methyacrylate was also observed upon pyrolysis, and there was a smaller amount of acetone. Methyl vinyl acetate and methyl crotonate were absent in the pyrolysis products.

The higher molecular weight fragments were numerous but have not been identified specifically. They contain more than six carbon atoms in the chain. In the case of H-H poly(methyl acrylate) the

expected dimethyl adipate was not among the degradation products although we looked especially for this compound.

When H-H poly(methyl cinnamate) was pyrolyzed under similar conditions, the major product was methyl cinnamate (about 80°). One other pathway of pyrolysis was degradation to the monomers from which the polymer was prepared by alternating copolymerization, namely, stilbene and a mixture of dimethyl maleate and dimethyl fumarate. In the case of the pyrolysis of H-H poly(methyl acrylate), it was expected that the pyrolysis of this polymer would form at least some of the monomers from which the H-H polymer was originally prepared. In spite of careful studies, we were unable to detect any of these products: ethylene, and the transformation product of maleic anhydride, dimethyl maleate or dimethyl fumarate, even in trace amounts.
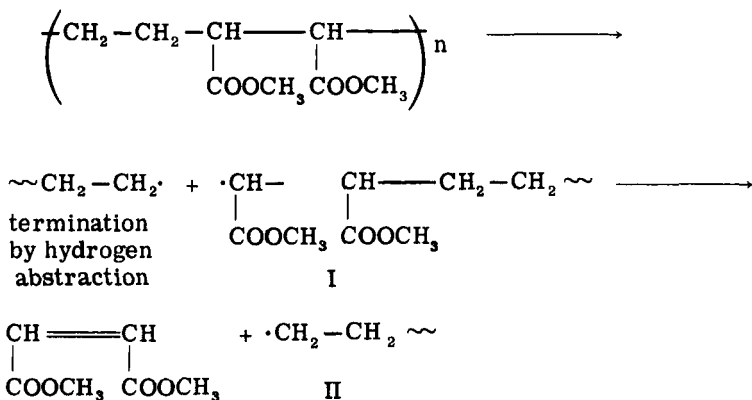
It is not surprising to find a substantial difference in the degradation pattern of poly(methyl acrylates) as compared to the previously described poly(methyl cinnamates). First of all, the maximum degradation temperature of poly(methyl acrylates) is approximately 50° higher than that of poly(methyl cinnamates), and the pyrolysis temperature of the two types of polymers tends to be different. As a consequence, reactions other than degradation to monomer, as in the case of poly(methyl cinnamate), began to occur when poly(methyl acrylate) was pyrolyzed above 400°C. As a consequence of this high pyrolysis temperature, we found larger amounts of carbon monoxide and methanol in the pyrolysis products than in simple methyl ester pyrolysis at these temperatures [11].

The relative stability of the intermediate degrading polymeric radicals during pyrolysis of poly(methyl cinnamate) and poly(methyl acrylate) is substantially different. All polymeric radicals formed from poly(methyl cinnamate) have either a phenyl or a carboxymethyl substituent on the terminal degrading polymeric radical. These radicals are resonance stabilized and are not expected to abstract hydrogen atoms readily from any other part of the molecule but are expected to form monomer upon degradation [12].

During the thermal degradation of poly(methyl acrylate), very reactive polymeric radicals with methylene groups at the end of the polymer chain are formed. These radicals are capable of abstracting hydrogen from any other portion of the molecule or from other molecules to form methyl-terminated polymer fragments. At the same time, new polymeric radicals are formed which can undergo further degradation.

One of the weak points in the polymeric chain is created by preferentially abstracting the tertiary hydrogen which is attached to the carbomethoxy group, therefore facilitating the formation of CO_2 and methanol.

One of the possible breakages of the polymer chains which would account for the C4 fragment which were observed is

$$\left(CH_2-CH_2-\underset{\underset{COOCH_3}{|}}{CH}\underline{\quad\quad}\underset{\underset{COOCH_3}{|}}{CH}\underline{\quad\quad} \right)_n \quad\quad\longrightarrow$$

$$\sim CH_2-CH_2\cdot \;+\; \cdot\underset{\underset{COOCH_3}{|}}{CH}-\quad \underset{\underset{COOCH_3}{|}}{CH}\underline{\quad\quad}CH_2-CH_2 \sim \quad\quad\longrightarrow$$

termination
by hydrogen
abstraction   I

$$\underset{\underset{COOCH_3}{|}}{CH}\underline{\quad\quad}\underset{\underset{COOCH_3}{|}}{CH} \quad + \;\cdot CH_2-CH_2 \sim$$

                                    II

The formation of dimethyl maleate and the polymeric methylene
radical, II, from the dimethyl maleate terminated radical, I, would
require the loss of dimethyl maleate from a stable polymeric
radical to form an unstable methylene terminated polymeric radical
and dimethyl maleate, which is unlikely. Primarily, fragmentation
to small molecules occurs in addition to the formation of 60% char.

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