

# Letters

## Structures of dimers formed from poly(barium methacrylate)

One of us previously reported<sup>1-3</sup> that metal salts of poly(methacrylic acid) decompose at 500°C to give products consisting mainly of five-membered cyclic ketones. We have been investigating the mechanism by which this metal salt affords five-membered cyclic ketones (dimethyl cyclopentanone, dimethyl cyclopentenone and methyl cyclopentanone, etc.).

Heat treatment of poly(barium methacrylate) (PBaMA) at 250°–300°C under a nitrogen stream resulted in a significant decrease of molecular weight without production of volatile decomposition materials. From the results of molecular weight decrease experiments it was concluded that the carbon-carbon main chain of the polymer undergoes random scission<sup>4</sup>. However, investigation of the structure of lower molecular weight products yielded from the PBaMA under the conditions described above has not yet been carried out.

We have studied an oligomer formation during an early stage of thermal decomposition of PBaMA. Here, we should like to report an interesting result obtained.

Freshly distilled methacrylic acid was polymerized in an aqueous solution in the presence of potassium persulphate as an initiator. The polymer was reprecipitated from ethanol solution by addition of a large amount of ether and then dried ( $\bar{M}_v$ , 85 000).

To 5% aqueous solution of barium hydroxide heated at 60°–70°C was added 10% aqueous solution of the poly(methacrylic acid) under vigorous agitation. Precipitate of PBaMA was collected and dried. Barium content of PBaMA: found, 39.95%. Calculated for  $(C_8H_{10}O_4Ba)_n$ , 44.66%.

PBaMA (294 G) was heated in a nitrogen stream at 330°C for 27 h. The heat-treated polymer salt was extracted with cold water. The soluble part (98 g), which may contain a lower molecular weight polymer salt, was acidified, extracted with ether and then esterified with diazomethane. The product (48.6 g) obtained thus, was distilled into two fractions and high boiling residue. The first fraction (b.p. 40°–110°C, 8 g) was consisted of ether and a small amount of the monomer identified by the gas chromatogram. The second fraction (b.p. 52°–145°C/4 mmHg, 25 g) is expected to be dimer and trimer fraction. There remained 15.6 g of high boiling residue.

From the gas chromatogram, the second fraction contains about 60% of a single component, and this component is determined to be a dimer by elution time on gas chromatogram. The yield of the dimer was calculated to be 6.8% based upon heat-treated PBaMA.

In order to assign the structure of the dimer, a fraction of pure single component (b.p. 109°–110°C/8 mmHg) was obtained from the second fraction by fractional distillation.

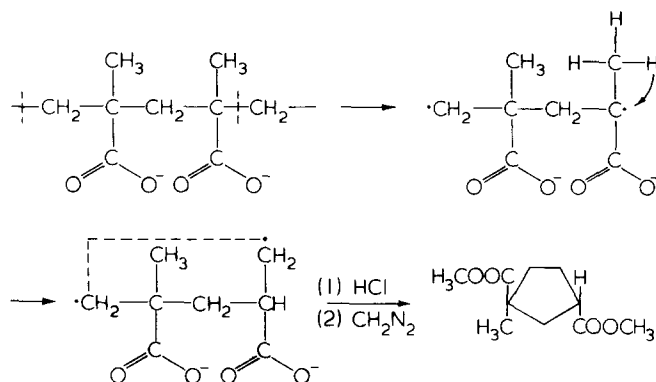
A mass spectrum of this component exhibited peaks at  $m/e$  200 ( $M^+$ ), 169 (23), 41(52), 109 (63), 81 (100). An n.m.r. spectrum showed peaks at  $\delta$  1.22 (s, 3H), 2.80 (q, 1H), 3.59 (s, 3H) and 3.60 ppm (s, 3H), and correspond in chemical shifts to the groupings  $-CH_3$ ,  $\rightarrow CH$ ,  $-OCH_3$  and  $-OCH_3$ , respectively. In the i.r. spectrum, stretching of  $\nu C=O$  was

observed at 1740  $cm^{-1}$ . From these spectra, the structure of the dimer was assigned as dimethyl 1-methyl-1,3-cyclopentanedecarboxylate (I).

Dauben and coworkers<sup>5</sup> synthesized dimethyl 1-methyl-1,3-cyclopentanedecarboxylate (II) starting from 1-methylnorbornene by treatment of ozonide with hydrogen peroxide and subsequent esterification with diazomethane. The mass and n.m.r. spectra of (I) agreed with those reported by Duban except for peaks due to ester group.

Stretching of  $\nu C=O$  was observed at 1740  $cm^{-1}$  in (I), but at 1745  $cm^{-1}$  in (II). In the n.m.r. spectrum, peaks for the protons of methoxy carbonyl groups are slightly shifted to higher magnetic field in (II) [ $-OCH_3$  3.48 (s, 3H) and 3.5 ppm (s, 3H)], compared with (I) [ $-OCH_3$  3.59 (s, 3H)] and 3.60 ppm (s, 3H). Therefore, (II) may be estimated to be *cis*-form. If this is true, (I) may be considered to be *trans*-form. Exact assignment of steric structure of (I) will be carried out in the near future.

It is interesting that (I) is formed exclusively as the dimer in the early stage of the thermal decomposition of PBaMA. The scission of the polymer is performed randomly<sup>4</sup>, and resulting fragments cannot vaporize since these are bound to barium ions by ionic bonds. When the decomposition proceeds to produce a biradical of dimeric unit, hydrogen migration and cyclization occur to form a cyclopentane derivative as follows.



However, there may be considered several kinds of reaction mechanisms for the oligomer formation from these polymer salts. We are on the way of a study for further evidence.

Kiyoshi Naruchi, Osamu Yamamoto,  
Masatoshi Miura and Kuniharu Nagakubo

Department of Industrial Chemistry, Faculty of Engineering,  
Chiba, Japan

(Received 31 August 1978)

## REFERENCES

- 1 Furukawa, S., Miyazawa, S. and Naruchi, K. *Chiba Daigaku Kogakubu Kenkyo Hokoku* 1963, 14, 39
- 2 Furukawa, S. and Naruchi, K. *Ibid.*, 1965, 16, 83
- 3 Furukawa, S., Naruchi, K. and Kumagawa, N. *Ibid.* 1966, 17, 33; *Chem. Abstr.* 1966, 65, 15518d
- 4 Naruchi, K., Ohashi, K., Niura, M. and Nagakubo, K. *Nippon Kagaku Kaishi* 1977, p 99; *Chem. Abstr.* 1977, 86, 90533d
- 5 Dauben, N. B. and Aoyagi, E. I. *J. Org. Chem.* 1972, 37, 258