Structure and polymerization conditions of poly(methyl vinyl ketone)

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The products of polymerization of methyl vinyl ketone with benzoyl peroxide, sodium and sodium tertiary butoxide were compared using u.v, i.r, n.m.r. and viscosities. With sodium and sodium t-butoxide, poly(methyl vinyl ketone) is partly cyclized forming polyunsaturated ketone. The degree of cyclization of the polymer obtained with sodium t-butoxide is higher than that with sodium, and the viscosity of the solution in acetone was also higher. The mechanism of cyclization is discussed in each case.

INTRODUCTION

The polymerization of methyl vinyl ketone has been extensively studied, and the properties of the polymer and its copolymers have attracted attention because of their importance in some industrial applications[1,2]. It is known that methyl vinyl ketone undergoes photopolymerization[10]; it has been shown that it polymerizes by a free radical and also by an anionic[3,4] mechanism. It is also known that poly(methyl vinyl ketone) does not have much heat resistance and exhibits a change in structure due to cyclization involving adjacent groups, when heated to 260°–270°C. The polymer also undergoes cyclization forming polyunsaturated ketone when treated with alkali[5] and phosphoric acid[6]. It is not known however how cyclization is affected by the polymerization conditions, especially at low temperatures. In this communication we compare the structure of the polymer which results from different polymerization conditions using benzoyl peroxide, sodium, and sodium t-butoxide as catalysts. This is achieved by examining the u.v., i.r. and n.m.r. spectra.

EXPERIMENTAL

Polymerization of methyl vinyl ketone with sodium was carried out as follows. Freshly distilled methyl vinyl ketone (5 ml) was dissolved in *N,N*-dimethylformamide (5 ml). After cooling to 5°C sodium metal (0.1 g) was added, the solution stirred for 70 min under nitrogen, and water then added to precipitate the polymer. The polymer was purified by dissolution in acetone and reprecipitation with cyclohexane. The yellow solid was dried *in vacuo* at 70°C, m.p. 170°–195°C. Calculated for C_4H_6O: 68.54% C, 8.62% H; found: 70.75% C, 8.45% H. The polymer was soluble in alcohol, chloroform, and acetone; it was insoluble in water.

Polymerization with sodium t-butoxide was carried out as follows. Freshly distilled methyl vinyl ketone (5 ml) was dissolved in toluene (25 ml). The solution was heated to 95°–100°C, and sodium t-butoxide, freshly prepared from sodium metal (0.1 g), and t-butanol (5 ml) were added. The reaction was continued for 5 h at 95°–100°C with stirring. The solvent was removed under reduced pressure and the residue dissolved in a little acetone and reprecipitated with water. The pale yellow transparent gum, purified by redissolving it in acetone and precipitating with water, was dried *in vacuo* at 70°C, m.p., 110°–125°C.

Polymerization of methyl vinyl ketone with benzoyl peroxide was carried out using the method reported by Sorenson and Campbell[9]. The i.r. spectra were measured with a Perkin–Elmer 257 spectrophotometer, the n.m.r. spectra with a Varian T-60A using TMS as a standard.

RESULTS AND DISCUSSION

When methyl vinyl ketone in dimethylformamide was polymerized with sodium metal at 5°C in an inert dry atmosphere an orange precipitate was obtained, a gelatinous white solid was obtained with benzoyl peroxide polymerization. When methyl vinyl ketone in toluene is polymerized with sodium t-butoxide at 95°–100°C a pale yellow gum is obtained. This polymer forms a hard transparent film from toluene, and has lower melting point and higher viscosity than that obtained with sodium. The polymerization with sodium was repeated at 25° and at 95°C, and it was found that the viscosity of the polymer increased with the increase in polymerization temperature. The results are summarized in *Table 1*.

Table 1 Stretching vibration (cm^{-1}) in chloroform of the main peaks at the same concentration

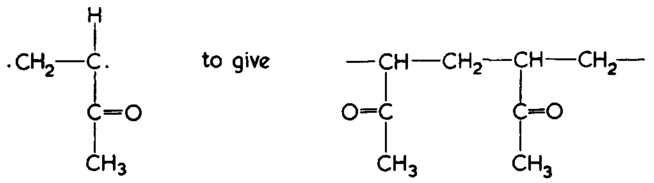
	C–H (aliphatic)	C=O	O–H (bonded)	C=C	M.p. (°C)	η_{sp}/c in acetone at 25°C
Methyl vinyl ketone	–	1680 (vs) 1710 (sh)	3420 (vs) (broad)	1620 (m)		
Polymerized with peroxide (A)	2910 (s)	1710 (vs)	–	–	140–160	0.197
Polymerized with sodium (B)	2910 (s)	1710 (vs)	3420 (m)	1660 (s) 1620 (sh)	170–195	0.234
Polymerized with t-butoxide (C)	2910 (m)	1700 (vs)	3420 (m)	1660 (vs) 1620 (sh)	110–125	0.242

vs, very strong; s, strong; m, medium; sh, shoulder

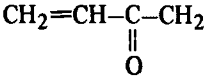
Polymers B and C showed two main bands: one at 3420 cm^{-1} characteristic of a bonded O–H stretching vibration and another at 1660 cm^{-1} characteristic of a C=C stretching vibration; such bands were absent from the spectra of polymer A. A comparison of polymers B and C showed that the 1660 cm^{-1} band is more intense and the 2910 cm^{-1} band less intense in polymer C; moreover, the 1360 cm^{-1} band due to the C–H bending vibration of the methyl group is less intense in polymer C.

The n.m.r. spectra of polymers B and C in $CDCl_3$ both showed a weak peak at 4.13 τ due to an ethylenic proton, which was not shown in the spectra of polymer A. Both B and C showed a peak at 7.63 τ characteristic of a proton in $CH_3 - C = C$ but this peak was relatively much weaker in the spectra of polymer B. The spectra of the three polymers showed a peak at 7.83 τ characteristic of a proton in $CH_3 - C = O$, however this peak was strongest in the case of polymer A.

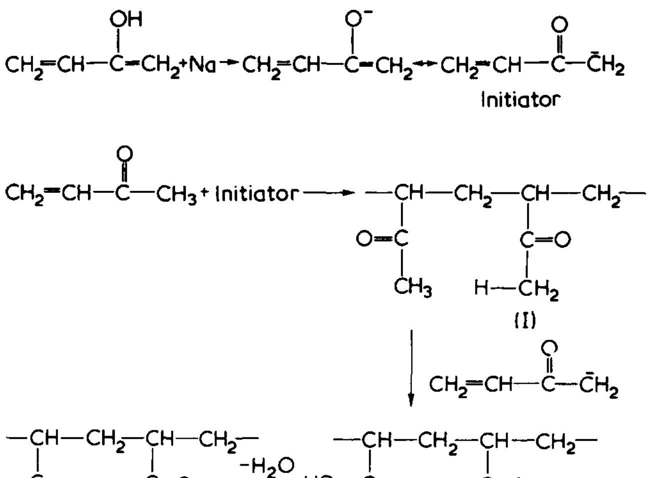
The polymerization of methyl vinyl ketone with benzoyl peroxide takes place through the formation of the free radical as would be expected.



However, the polymerization with sodium probably takes place through the anion

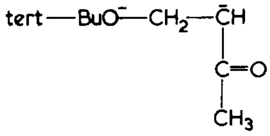

$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}\bar{C}H_2$$

which acts as the initiator to form the polymer with structure I. Then two adjacent groups in the polymer undergo cyclization. This is possible if we assume that the anion initiator acting as a base removes an active hydrogen from the methyl group, then cyclization takes place followed by a hydrogen transfer to the oxygen atom (structure II).

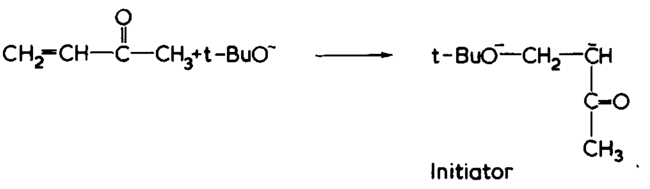


Some elimination of water must have occurred leading to a double bond formation (structure III) as indicated by the spectra, although the reaction was carried out at 5°C.

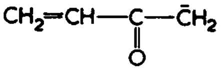
The polymerization of methyl vinyl ketone in the presence of sodium t-butoxide takes place through the anion



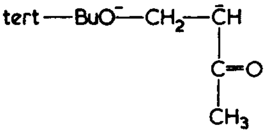
The polymer formed (structure I) then undergoes cyclization where the anion initiator itself probably acts as the base in the hydrogen transfer process. The elimination of water is now more likely since the reaction was carried out at 95°–100°C, and this leads to unsaturation (structure III). The u.v. spectra of chloroform solutions gave evidence of an unsaturated ketone: polymer B absorbs at 250 µm (ϵ 2900) and at 290 µm (ϵ 900); polymer C absorbs at 250 µm (ϵ 3150) and at 290 µm (ϵ 600).



The cyclization of polymers B and C must be only partial since the spectra indicate that some of the CH_3CO groups are still free. However, in polymer C the more intense band of the C = C in the i.r. spectra and the more intense band of the $CH_3 - C = C$ in the n.m.r. spectra indicates a higher degree of cyclization. This shows that the two anions:


$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}\bar{C}H_2$$

and



do not lead to the same degree of cyclization.

It must be recalled for comparison that t-butoxide acts as a base in the hydrogen transfer polymerization of acrylamide[7,8]; this leads to the straight chain poly(β-alanine) $-\!\!\left(CH_2-CH_2-CO-NH\right)\!\!-$.

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