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*Department of Applied Chemistry, Faculty of Engineering, Kinki University, Hiro-machi, Kure-shi, Hiroshima, 737-01 Japan and **Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan

Short Communication

Synthesis and Polymerization of 4-Aryliminomethyl-2-methoxyphenyl Methacrylates

Kazuo Sugiyama* and Tadao Nakaya**

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A great amount of interest has recently been shown in the vinyl monomers having liquid crystalline properties¹⁻¹¹. Cholesteryl acrylate^{3,4} and methacrylate^{5,6} have been prepared and polymerized. Schiff bases containing an acryloyl or methacryloyl group have also been synthesized and polymerized in solution as well as in the isotropic and anisotropic melt⁷.

The synthesis of a novel liquid crystalline vinyl monomer is of interest in connection with the above mentioned work which has already been published.



As part of a general survey on the synthesis and properties of such monomers, the authors have now prepared the 4-aryliminomethyl-2-methoxyphenyl methacrylates **1a-d**.

They were polymerized in bulk or in carbon tetrachloride by 2,2'-azoisobutyronitrile (AIBN). The thermal properties of **1a–d** were also examined.

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Experimental Part

2-Methoxy-4-phenyliminomethylphenol and derivatives. General procedure: Vanillin (0,5 mol) and p-substituted aniline (0,5 mol) in 500 cm^3 of toluene were heated under reflux for 10 h, during which time ca. 0,5 mol of water was collected in the Dean-Stark trap. After removal of the solvent, the pure imines were obtained in about 90% yield by recrystallization from ethanol.

2-Methoxy-4-(phenyliminomethyl)phenol: mp 155-156°C (Lit.^{12a)}: mp 152-153°C).

2-Methoxy-4-(p-tolyliminomethyl)phenol: mp 118-121 °C (Lit.^{12b)}: mp 115,5°C).

2-Methoxy-4-(p-methoxyphenyliminomethyl)phenol: mp130-132°C (Lit.¹²⁰: mp 137°C).

2-Methoxy-4-(p-chlorophenyliminomethyl)phenol: mp 127-130°C.

2-Methoxy-4-phenyliminomethylphenyl methacrylate and derivatives. General procedure: Methacryloyl chloride (0,12 mol) was added dropwise to a stirred solution of one of the above phenol derivatives (0,1 mol), 300 cm^3 of chloroform, 40 cm^3 of triethylamine, and a catalytic amount of hydroquinone at 0°C. The additional stirring was continued for 3 h at room temp. 600 cm^3 of ice/water were added and the solution was extracted with chloroform. The extract was washed three times with 1 M hydrochloric acid and then with water. After drying over sodium sulfate, the solution was filtered and evaporated i. vac. The product was distilled under reduced pressure.

2-Methoxy-4-phenyliminomethylphenyl methacrylate (1a): bp 137-140°C (≈ 2 mbar); yield 80,4%. - NMR (CCl₄): $\delta = 2,45$ (s; -CH₃), 4,60 (s; -OCH₃), 7,30 (d; CH₂==), 8,20-9,24 (m, aromatic 8 H), and 9,84 ppm (s, -CH=N-). - IR (KBr): v = 1740 (C=O), 1655 (CH₂=C \leq), 1630 (-CH=N-), and 880 cm⁻¹ (CH₂=C \leq).

C ₁₈ H ₁₇ NO ₃ (295,3)	Calc.	C 73,20	H 5,80	N 4,74
*	Found	C 73,5	H 5,4	N 4,7

2-Methoxy-4-(*p*-tolyliminomethyl)phenyl methacrylate (**1b**): bp 140–145 °C (≈ 2 mbar); yield 66,3%. – NMR (CCl₄): $\delta = 2,48$ (s; —CH₃), 2,79 (s; —CH₃), 4,62 (s; —OCH₃), 7,32 (d; CH₂=), 8,24–9,24 (m; aromatic 7H), and 9,63 ppm (s; —CH=N—). – IR (KBr): $\nu = 1740$ (C=O), 1650 (CH₂=C \leq), 1630 (—CH=N—), and 878 cm⁻¹ (CH₂=C \leq).

C ₁₉ H ₁₉ NO ₃ (309,4)	Calc.	C 73,77	H 6,19	N 4,51
	Found	C 74,0	H 6,0	N 4,8

2-Methoxy-4-(*p*-methoxyphenyliminomethyl)phenyl methacrylate (1c): bp 125-130°C (≈ 2 mbar); yield 67,0%. - NMR (CCl₄): $\delta = 2,44$ (s; --CH₃), 4,60 (s; --OCH₃), 7,24 (d; CH₂=), 8,40-9,20 (m; aromatic 7H), and 9,90 ppm (s; --CH=N-). - IR (KBr): v = 1740 (C=O), 1652 (CH₂=C \leq), 1635 (--CH=N-), and 878 cm⁻¹ (CH₂=C \leq).

C ₁₉ H ₁₉ NO ₄ (325,4)	Calc.	C 70,14	H 5,89	N 4,31
	Found	C 70,9	H 6,0	N 4,5

2-Methoxy-4-(*p*-chlorophenyliminomethyl)phenyl methacrylate (1d): bp 144–149°C (\approx 2mbar); yield 40,5%. – NMR (CCl₄): δ =2,40 (s; –-CH₃), 4,60 (s; –-OCH₃), 7,40 (d; CH₂==), 8,20–9,40 (m; aromatic 7H), and 9,85 ppm (s; –-CH=N–). – IR (KBr): ν =1740 (C=O), 1655 (CH₂==C \leq), 1640 (--CH=N–), and 890 cm⁻¹ (CH₂==C \leq).

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C ₁₈ H ₁₆ ClNO ₃ (329,9)	Calc.	C 65,57	H 4,89	N 4,25
	Found	C 65,1	H 4,7	N 4,2

Polymerization procedure: 1a-c were polymerized in pure state in bulk or in carbon tetrachloride by AIBN in degassed sealed tubes with shaking in a thermostat maintained at 50 °C. The products were isolated by pouring the reaction mixture into an excess of methanol.

Differential thermal analyses (DTA): DTA of 1a-d were carried out with a "Rigaku Denki" DTA instrument. The experimental conditions were as follows: mg-scale, 5 (1b, 1c) and 10 (1a, 1d); TG range: 5 mg; DTA range: $\pm \mu V$; temp. recorder: 5 mV; an Al-dish was used.

Measurements of mp: mp were measured with a "Yanagimoto" micro melting apparatus.

Results and Discussion

In order to check whether 1a-d show liquid crystalline properties their DTAs were carried out under nitrogen. Fig. 1 shows the two endothermic peaks which are due to the phase transformations solid state \rightarrow liquid crystalline state \rightarrow isotropic phase. The anisotropic phases exist from 38 to 39 °C, from 41 to 42 °C, and from 48 to 52 °C for 1a, 1b, and 1c, respectively. It is of interest to show that the anisotropic phases exist at very low temperatures, but in a narrow temperature range. This was confirmed by observations using a polarized light microscope. 1a-1c were found to be nematic liquid crystalline vinyl monomers. In the case of 1d, liquid crystalline properties were not observed by any method.



Fig. 1. DTA curves of 1a-c

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There are some reports concerned with the polymerization of vinyl monomers having liquid crystalline nature. The effect of liquid crystalline phase on the overall polymerization rate of vinyl monomers have been studied in the anisotropic and isotropic melt. It has been found that the rate of polymerization depends on the polymerization condition in the case of vinyl oleate¹⁾ cholesteryl methacrylate⁶⁾, and several acryloyl and methacryloyl substituted schiff bases¹¹⁾. On the other hand, the polymerization rates of 5-alkoxy-2-(p-vinylphenyliminomethyl)phenol⁸⁾ and of cholesteryl acrylate⁴⁾ were independent of the polymerization conditions. The information is required to establish the effects of an anisotropic phase on the rate of polymerization. In this connection, the polymerization of **1a-c** initiated by AIBN was carried out in bulk at 50°C as shown in Fig. 2. At this reaction temperature 1a and 1b are in an isotropic melt, whereas 1c is in an anisotropic one. The order of the overall polymerization rates is as follows: 1a > 1c > 1b. It is known that the polymerization rate of a vinyl monomer is increased by introducing electron donating substituents into the monomer¹³). Accordingly, the order of polymerization rate is expected to be as follows: 1a > 1b > 1c. The experimental results indicate that the rate of polymerization of 1c increases due to an ordered matrix state¹⁾.



Fig. 2. Polymerization of 1a-d initiated by AIBN in bulk at 50°C; AIBN=0,02 g; 1=1,00 g. (•): 1a; (\circ): 1c; (\triangle): 1b

The polymerization of 1a-c with AIBN was also carried out in carbon tetrachloride at 50°C as shown in Fig. 3.

Comparing the overall polymerization rate in bulk and in carbon tetrachloride, **1a-c** show the highest conversions (e.g. after 80 min reaction time) in bulk polymerization, their overall polymerization rates decrease in carbon



Fig. 3. Polymerization of 1a-c initiated by AIBN in CCl₄ at 50 °C. AIBN = 0,02 g; 1 = 1,00 g; CCl₄ = 5 ml. (\bullet): 1a; (Δ): 1b; (\circ): 1c

tetrachloride. This result may be explained on the basis of the same above mentioned reason. It is suggested that 1c exists in a highly oriented state even in solution.

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