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Copolymerization of Allilidene Diacetate with Vinyl Acetate

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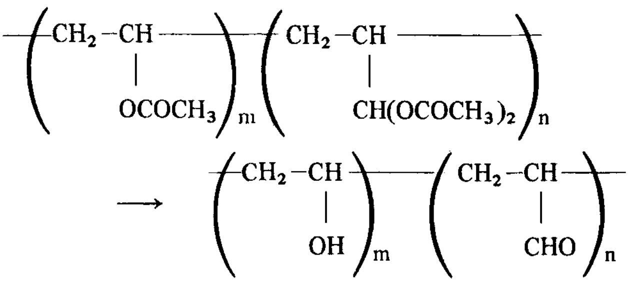
SUMMARY

The monomer reactivity ratios for vinyl acetate (VAc)-allilidene diacetate (ADA) copolymerization have never been obtained. The composition of VAc-ADA copolymers was determined by NMR spectroscopy, measuring CH protons corresponding to ADA at 3.1τ and VAc at 5.1τ. The monomer reactivity ratios were evaluated: $r_1 = 1.34 \pm 0.05$ and $r_2 = 0.48 \pm 0.03$, where M_1 = ADA and M_2 = VAc. From these values the Q and e values for ADA were calculated: $Q = 0.047$ and $e = 0.44$ by taking $Q = 0.026$ and $e = -0.22$ for VAc. The H value [1] for copolymerization of ADA, VAc, and vinyl chloride (VC) is 0.87.

INTRODUCTION

The copolymerizations of ADA with styrene [2], VAc [3], and VC [4] have been reported, but only the ADA-VC copolymerization has been studied in detail. The present paper deals with the copolymerization of ADA with VAc. The elemental analysis of the resulting polymers could not be used to determine copolymer composition, since both monomers have almost the same elemental analysis. Saponification of the copolymer was investigated for the determination of the composition of the copolymer [5].



$$\left(CH_2-\underset{OCOCH_3}{CH}\right)_m\left(CH_2-\underset{CH(OCOCH_3)_2}{CH}\right)_n \longrightarrow \left(CH_2-\underset{OH}{CH}\right)_m\left(CH_2-\underset{CHO}{CH}\right)_n$$

It was found that the measurement of the resulting carbonyl group by the hydroxyl amine or bisulfite method gave consistently low values. Consequently, NMR spectroscopy was found adaptable to the determination of copolymer composition. The results were in good agreement with those from the determination of unreacted monomers by gas chromatography (GC).

EXPERIMENTAL

Materials

ADA was prepared from acrolein and acetic anhydride: bp 85°C/20 mm Hg [2]. Its purity was determined to be 99.8% by GC. (A 2-m column filled with PEG 20 M at 150°C, He flow 30 ml/min).

Isobutylidene diacetate (IBDA) was prepared from isobutyraldehyde and acetic anhydride: bp 89°C/20 mm Hg. The purity was 99.7% by GC. (Column as above). Acetone, n-hexane, petroleum ether, and VAc (all commerical grades) were purified by distillation. Acetone impurities were 0.001% acetic acid and 0.05% water, and VAc impurities, 0.003% acetaldehyde, 0.001% acetic acid, and 0.04% water according to the Japanese industrial standard method (JIS K 8031-1961 and 6724-1956).

Reagent grade azobis-isobutyronitrile (AIBN) was recrystallized from methanol.

Polymerization Procedure

A mixture of ADA, VAc, and AIBN was placed with a hypodermic syringe. The ampoule was then connected with a vacuum system and, after degassing, sealed off under vacuum. Polymerizations and copolymerizations were carried out in a constant-temperature bath (±0.1°C). After polymerization the contents of the ampoule were poured into a large amount of petroleum ether in order to precipitate the polymer. The polymer was washed thoroughly with petroleum ether, filtered, dried under vacuum at 60°C, and weighed. The rate of polymerization was estimated from the amount of dried polymer obtained. Induction time is defined as the value at which the time axis is intersected by the line of steady rate of polymerization.

Analysis of the Polymer

The composition of the copolymers was determined by NMR spectroscopy of the CH proton region. A Japan Electron Optics C-60 HL spectrometer (60 Mc/sec) was used. Measurements were done at 60°C, and 10% polymer solution in $CDCl_3$ with 2% of tetramethylsilane was used as the internal reference. The intrinsic viscosity of the polymers was determined in acetone solution at 30°C.

Analysis of Unreacted Monomers

A 2-g portion of a reaction mixture was accurately weighed into a 100-ml glass stoppered flask containing about 25 ml of n-hexane and then weighed. The amount of ADA in the supernatant was determined by GC. The column (3 mm X 2 m, packed with 60-80 mesh Chromosorb W and containing 10% by weight of SE-52,) was operated at 120°C with a helium flow rate of 30 ml/min and used IBDA as the internal reference. The amount of VAc was determined with a column, 3 mm X 2 m, packed with 80-100 mesh Porapak Q and operated at 120°C, with a helium flow rate of 30 ml/min, using acetone as the internal reference.

RESULTS AND DISCUSSION

The NMR Spectra of Homo- and Copolymers

The NMR spectra at 60°C of polyallilidene diacetate (PADA) and the copolymer of ADA with VAc in $CDCl_3$ are shown in Fig. 1. The polymers were prepared by bulk polymerization with AIBN initiator at 60°C. Tau values of PVAc protons of CH, CH_3, and CH_2 were found to be 5.1, 8.0, and 8.2 [6] and those of PADA were 3.1, 7.95, and 8.5, respectively. IBDA, whose peaks appeared at $3.4\tau(-\mathrm{CH}{<}{-}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}})$, $7.95\tau(CH_3CO_2-)$, 9.06τ (CH_3-), and about $8\tau(\mathrm{CH}{<}-)$, was used as the reference compound to assign the peaks of PADA. The composition of the copolymer was evaluated from the ratio of area of the peaks 3.1τ and 5.1τ. The standard deviation in the mole per cent determination of the copolymer was ±1.1, as shown in Table 1.

Copolymerization of ADA with VAc

The results of the radical copolymerization of ADA with VAc, initiated by AIBN, are summarized in Tables 1-3, and the monomer-copolymer composition curve from Table 1 is shown in Fig. 2.

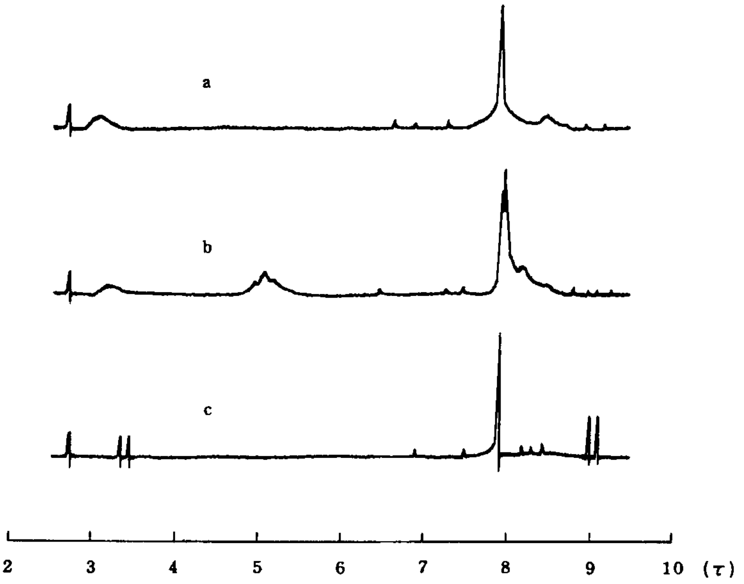


Fig. 1. NMR spectra in $CDCl_3$ at 60°C. (a) Polyallilidene diacetate, (b) copolymer of allilidene diacetate with vinyl acetate (Run 3 in Table 1), (c) isobutylidene diacetate.

Table 1. Composition of Copolymers of ADA (M_1) with VAc (M_2)

Run no.	AIBN to monomer mixture, mole %[a]	M_1 in monomer mixture, mole %[a]	Time, min	Yield, wt %	m_1 in copolymer, mole %[a]	
1	0.1	5.74	10	4.50	10.1	11.3
2	0.1	7.28	10	2.59	11.9	13.5
3	0.1	19.4	20	5.56	26.2	27.8
4	0.1	34.4	20	3.57	43.3	44.1
5	0.1	51.8	30	6.42	63.8	65.6
6	0.1	54.9	30	3.34	63.9	65.3
7	0.2	66.4	30	6.17	76.7	78.3
8	0.3	84.2	30	5.88	87.7	88.3

[a] The standard deviation in the mole % determinations was ±1.1 based on 8 degrees of freedom.

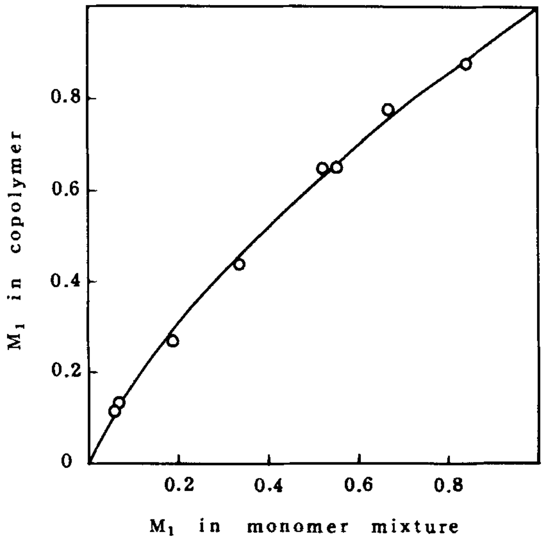


Fig. 2. Monomer-copolymer composition curve for allilidene diacetate (M_1)-vinyl acetate (M_2) copolymerization initiated by AIBN at 60°C. ○ = observed, — = calculated from $r_1 = 1.34$, $r_2 = 0.48$.

The Monomer Reactivity Ratios and the Q and e Values

The monomer reactivity ratios with standard deviations were calculated according to the Fineman-Ross method, using a Melcom 3100 computor with the Fortran program developed by Harwood et al. [7].

$$M_1 = \text{ADA} \quad M_2 = \text{VAc} \quad r_1 = 1.34 \pm 0.05 \quad r_2 = 0.48 \pm 0.03$$

The values were also confirmed from the results of large-scale polymerization in which monomers that remained unreacted were determined by GC as shown in Table 3. The Q and e values for ADA were calculated by using Q = 0.026 and e = -0.22 for VAc:

$$Q = 0.047 \qquad e = 0.44$$

They are in fairly good agreement with the values of Ohta et al. [4]: Q = 0.026 and e = 0.2 obtained from the copolymerization of ADA with VC. The H value for copolymerization of ADA, VAc, and VC is nearly

Table 2. Results of Copolymerization of ADA (M_1) with VAc (M_2). (AIBN) = 0.02 mole % to monomer mixture.

Run no.	M_1 in monomer mixture, mole %	Time, min	Yield, wt %	Rate of copolymerization, wt %/min	m_1 in copolymer, mole %	Intrinsic viscosity, dl/g	Induction time, min
11	0.0	70	16.0	0.276	0.0	1.52	12
12	5.3	95	20.5	0.244	6.9	1.27	15
13	11.0	131	21.6	0.213	15.6	1.10	22
14	21.9	155	19.8	0.151	31.6	0.69	35
15	32.1	216	21.9	0.128	41.7	0.59	40
16	42.7	328	25.1	0.094	50.7	0.49	60
17	62.5	628	22.8	0.05	64.2	0.30	145
18	79.7	1402	25.6	0.023	85.3	0.24	280
19	100.0	5101	29.7	0.007	100.0	0.13	350

Table 3. Copolymerization of ADA with VAc in Methanol at 60° C

Time, min		240	300	390
Conversion [b], %	ADA	86.3	90.7	94.8
	VAc	60.9	78.5	85.2

[a] ADA, 110 g; VAc, 340 g; methanol, 150 g; AIBN, 0.03 mole % to monomer mixture.

[b] Calculated from GC analysis of unreacted monomers in the reaction mixture.

unity. This fact indicates the validity of the above Q and e values.

M_1 = ADA ADA-VAc $r_{12} = 1.34$ $r_{21} = 0.48$
M_2 = VAc VAc-VC [8] $r_{23} = 0.23$ $r_{32} = 1.68$
M_3 = VC VC-ADA [4] $r_{31} = 1.75$ $r_{13} = 0.58$

$$H = \frac{r_{21} \times r_{32} \times r_{13}}{r_{12} \times r_{23} \times r_{31}} = 0.87$$

Rate of Copolymerization, Intrinsic Viscosity, and Induction Time

Both the rate of copolymerization and the intrinsic viscosity markedly decrease and the induction time increases as the concentration of ADA increases (Fig. 3). This is because an allylic radical can be formed readily from ADA. The allylic radical $\dot{C}H_2CH\dot{C}(OCOCH_3)_2$ formed by radical chain transfer to ADA may be very stable [9, 10]. This degradative chain transfer step is, effectively, the termination step; therefore, both copolymerization rate and intrinsic viscosity show the same tendency, as shown in Fig. 3. The Q and e values do not explain why ADA is more reactive than VAc in copolymerization but less reactive in homopolymerization.

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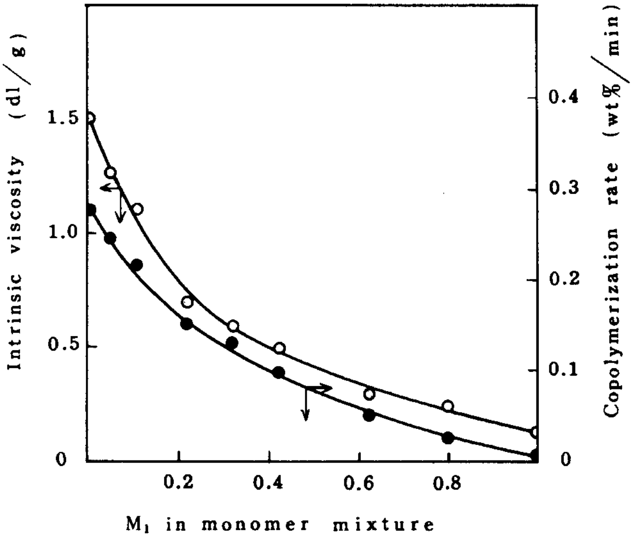

Fig. 3. Relationship among intrinsic viscosity, copolymerization rate, and monomer concentration for copolymerization of allilidene diacetate (M_1) with vinyl acetate (M_2).

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