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NOTE

CHARACTERIZATION AND THERMAL STUDIES OF COPOLYMERS OF METHYL METHACRYLATE AND MALEIC ANHYDRIDE PREPARED BY CHARGE-TRANSFER INITIATION

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INTRODUCTION

Charge-transfer (CT) polymerizations of vinyl monomers have been studied extensively in this laboratory [1-5]. Maleic anhydride (MAN) can initiate the CT polymerization of styrene in the presence of such solvents as ethylbenzene, cymene, and *p*-cymene [6]. However, in the presence of conventional initiators, MAN copolymerizes with methyl methacrylate (MMA). Free-radical copolymerization involving MAN with 2,2'-azobisisobutyronitrile (AIBN) has been extensively studied [7, 8]. CT copolymerization of MMA and MAN has not been reported so far. Here we report the characterization and thermal studies of MMA/MAN copolymers prepared by the CT method.

EXPERIMENTAL

MMA, MAN, CCl₄, dimethylsulfoxide (DMSO), AIBN, and trimethylamine (TMA) were of analytical grade and were purified by standard procedures. Polymerizations were carried out in a two-limbed vessel. The first limb was filled with a mixture of MMA and MAN in DMSO at varying ratios and the

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second with the amine and CCl_4 in DMSO. The vessel was completely evacuated, then the contents of two limbs were mixed, and it was immediately put into a thermostat at $60 \pm 0.01^\circ\text{C}$. After the desired time, copolymer was precipitated with methanol. The residue was filtered, washed, dried, dissolved in chloroform, and reprecipitated with methanol. The intrinsic viscosity $[\eta]$ in chloroform was determined at 30°C with an Ubbelohde viscometer. The copolymer composition was estimated by determining its anhydride content [9, 10].

The reactivity ratios were evaluated by the Fineman-Ross (FR) [11] and Kelen-Tüdös (KT) [12] methods.

IR spectra were recorded with a Carl-Zeiss Specord 75 IR. ^{13}C -NMR spectra were recorded at 67.89 MHz with a Bruker WH-270 Pulsed Fourier-transform NMR spectrometer. The broad-band proton decoupling method was used throughout. A chemical shift range of -10 to $+240$ ppm was used, with deuteriochloroform as the reference (center of triplet = 77.1 ppm for tetramethylsilane). The pulse width was $15 \mu\text{s}$ and the pulse repetition time of 2 s.

Differential scanning calorimetric (DSC) data were obtained on 4-10 mg samples during first heating in air with a Mettler TA 3000. For some experiments fresh samples were annealed at the final melting temperature, and the thermograms were repeated. Thermogravimetric analysis (TGA) was done using a Perkin-Elmer thermal analyzer in air at a heating rate of $10^\circ/\text{min}$ on 5 ± 1 mg powder samples.

RESULTS AND DISCUSSION

The yield of copolymer increased with increasing MMA content in the feed, reaching the maximum value at $[\text{MMA}]/[\text{MAn}] = 0.9$. When $[\text{MMA}]:[\text{MAn}] > 11$, only homopolymer of MMA resulted. The intrinsic viscosity also followed a similar trend. $[\eta]$ ranged from 1.8 to 2.5 dL/g as the mole ratio varied from 0.7 to 10.8. Maximum $[\eta]$ was obtained for a mole ratio of 0.9. The corresponding value for a copolymer prepared with AIBN initiator was 0.5 dL/g, illustrating that the MW of the CT copolymers are higher than those made with free radicals. The polymers prepared by CT mechanism were easily processable and soluble in a number of common organic solvents like chloroform, dioxane, acetone, etc.

A strong band at 1760 cm^{-1} along with a weak band at 1825 cm^{-1} in the IR spectra of the copolymer showed the presence of the five-membered cyclic anhydride ring [13]. This was supported by two other bands at 1220 and 920 cm^{-1} . However, the copolymers were hygroscopic and, on standing

in humid air, carboxylic groups were produced by hydrolysis of anhydride units. When anhydrous conditions were not maintained, an extra band due to water appeared around 3400 cm^{-1} . This hygroscopic nature was similar with copolymers prepared by AIBN.

^{13}C -NMR spectra indicated the formation of a copolymer between MMA and MAn. Carbonyl groups from both MMA and MAn showed overlapping low-field resonances at $\delta 177\text{--}178$ ppm. Methylene, methyl, and quaternary carbons from MMA units showed high-field resonances at $\delta 52.9\text{--}54.6$, $\delta 16.9\text{--}19$, and $\delta 44.8\text{--}45.1$ ppm, respectively. The peak at $\delta 51.7$ ppm corresponds to methoxy carbons in MMA units. The resonances at $\delta 39.0\text{--}41.1$ ppm are due to methine carbons in MAn units.

Reactivity ratios (MMA = M_1 , MAn = M_2) were as follows. FR method: $r_1 = 3.05 \pm 0.02$; $r_2 = 0.03 \pm 0.01$. KT method: $r_1 = 3.15 \pm 0.05$; $r_2 = 0.03 \pm 0.02$. The FR plot is shown in Fig. 1.

To check the thermal stability of the copolymers, DSC (Table 1) and TGA (Table 2) curves were recorded in air. The melting process is a complex one, since the DSC traces showed a cluster of three peaks, especially when the MAn content was low, suggesting that the crystallinity of the virgin copolymers was higher when the MMA content was lower.

The thermograms obtained after annealing at the final melting temperature did not show melting endotherms, i.e., the thermal change at or near the fusion temperature was permanent. The double broad endothermic peaks observed for the virgin copolymers with higher MAn content were above the base line, indicating volatilization of entrapped solvent and moisture with progressive decomposition. Comparison of the DSC data of the copolymer with those of pure PMMA (MW 10 280) showed that incorporation of MAn increased the thermal stability. It was also found that the CT copolymers were more thermally stable than free-radical copolymers.

The three endothermic peaks were followed by an exothermic peak appearing near 400°C . Increasing MAn content increased the exothermic decomposition peak temperature. The loss was about 97% at 500°C . The activation energy for the thermal decomposition in air increased with increasing MAn content. The reaction order for the endothermic reactions approached unity, and for the exothermic peak it approached two. The DSC curves were recorded at heating rates varying from 2 to $40^\circ\text{C}/\text{min}$. Extrapolation to zero heating rate resulted in 40, 160, and 314°C for the three melting points of the copolymer with composition 78/22.

The copolymers decomposed in two stages, with the major portion decomposing in the second stage (see Table 2). The copolymers were stable up to 132°C . The first-stage weight loss (6-17%) might be due to volatile matters,

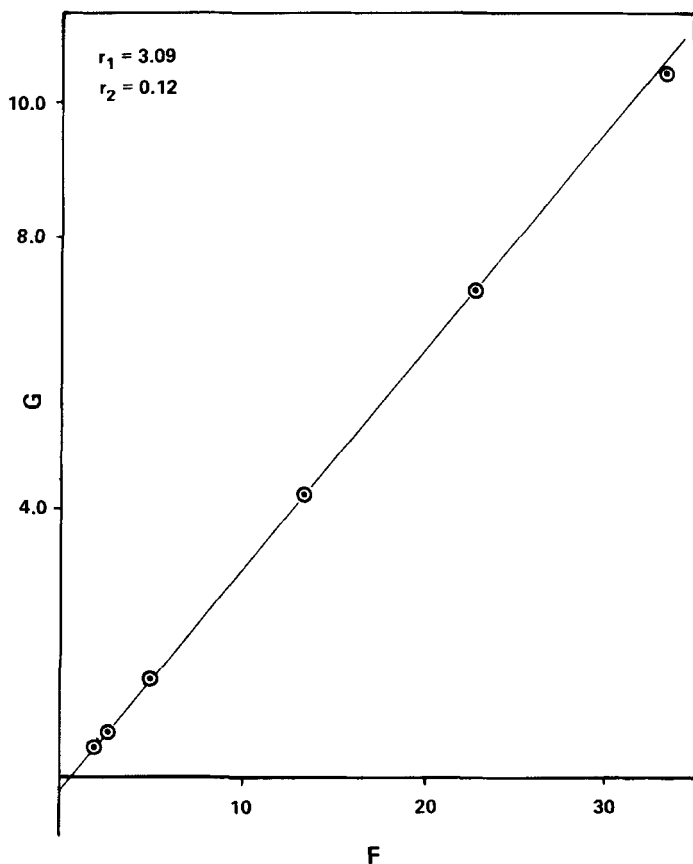


FIG. 1. Reactivity ratios of the MMA and MAN copolymer determined by the Fineman-Ross method. $G = [M_1]/[M_2]$ and $F = m_1/m_2$ where $[M_1]$ and $[M_2]$ are the molar concentrations in the monomer feed and m_1 and m_2 are the same in the copolymer.

entrapped solvent, and moisture incorporated in the polymer. Pure PMMA had higher initial thermal stability than the copolymers, while increasing MAN content in the copolymer decreased IDT_1 .

The amount of second-stage degradation varied between 81 and 89%. IDT_2 increased with the increasing MAN content. Thus, after removal of volatile matter, the incorporation of MAN to PMMA increased the thermal stability.

TABLE 1. Kinetic Data for MMA/MAn Copolymers and PMMA from DSC Study^a

Feed ratio [MMA]/[MAn]	Copolymer composition [MMA]/[MAn]	First endotherm			Second endotherm			Exotherm		
		Peak tempera- ture, °C	Order of reaction	Activation energy, kJ/mol	Peak tempera- ture, °C	Order of reaction	Activation energy, kJ/mol	Peak tempera- ture, °C	Order of reaction	Activation energy, kJ/mol
0.8	76/24	77.2	1.15 ± 0.07	101.6	370	0.93 ± 0.04	200	416	1.85 ± 0.26	865
0.9	78/22	76.0	1.20 ± 0.11	105.5	368	0.92 ± 0.07	168	412	2.02 ± 0.15	746
1.8	87/13	75.4	1.21 ± 0.05	113.9	367	0.85 ± 0.04	159	410	2.23 ± 0.25	543
4.5	94/6	69.8	1.11 ± 0.01	130.1	367	0.77 ± 0.07	152	408	1.92 ± 0.08	409
10.8	97/3	—	—	—	362	0.83 ± 0.05	153	405	2.12 ± 0.13	385
PMMA	100/0	—	—	—	360	0.93 ± 0.05	148	402	2.33 ± 0.21	273

^aHeating rate: 10°C/min, 50–500°C.

TABLE 2. Thermogravimetric Data for MMA/MAN Copolymers and PMMA^a

Feed ratio [MMA]/[MAN]	Copolymer composition [MMA]/[MAN]	IDT ₁ , ^b °C	IDT ₂ , ^b °C	% Weight loss			FDT, ^c °C	IPDT, ^d °C	
				100°C	200°C	300°C			
0.8	76/24	132	332	0.6	11.1	17.4	37.2	390	294
0.9	78/22	135	330	0.7	10.4	16.0	39.6	395	292
1.8	87/13	140	322	0.7	9.2	14.8	45.8	396	292
4.5	94/6	157	316	0.7	7.3	13.3	57.6	398	290
10.8	97/3	160	305	0.6	6.5	12.1	62.8	368	288
PMMA	100/0	165	295	0.5	4.2	15.9	71.7	363	286

^aHeating rate: 10°C/min.

^bIDT₁ and IDT₂ are initial decomposition temperatures for the first and second stages, respectively.

^cFDT is the final decomposition temperature.

^dIPDT is the integral procedural decomposition temperature [14].

For pure PMMA, the higher-temperature phase of degradation results from random scission that produces monomer [15]. In the copolymers, the presence of MAn in the backbone resisted random scission, thereby increasing IDT₂ and FDT. The char content after degradation was about 2%. For all the copolymers, maximum weight loss occurred in the range 300-400°C.

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