

Copolymerization of N-4-Dibenzoylmethane Maleimide with Styrene

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Abstract: The copolymer of N-4-dibenzoylmethane maleimide (*p*-DBMI) with styrene (St) was prepared and characterized by gel permeation chromatography, thermal analysis and spectroscopy.

Keywords: N-4-Dibenzoylmethane maleimide, styrene, copolymer.

β -Diketone compounds have unique photochemical and coordination chemical properties. Interest in polymeric β -diketone and its metal-containing polymers have been greatly stimulated by their potential use in photoresist¹, catalysis² and fluorescence and laser fields³. Thus there has been a trend towards the development of polymeric β -diketone. However, the maleimide-based copolymer containing β -diketone units has not been reported so far. In this paper, a novel copolymeric β -diketone was prepared by radical copolymerization of *p*-DBMI with St, the structure and property of which were characterized by gel permeation chromatography, thermal analysis and spectroscopy.

The *p*-DBMI was prepared from maleic anhydride and 4-aminodibenzoylmethane which was obtained by Claisen condensation reaction of 4-nitrobenzoic acid ethyl ester and acetophenone followed by reduction using 10% Pd/C⁴. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and used as initiator, St and dioxane were redistilled prior to use. Copolymerization was performed in ampoules under nitrogen at $65 \pm 0.2^\circ\text{C}$ using dioxane as solvent. Copolymers were recovered by precipitation in methanol, purified by reprecipitation from dioxane solution into methanol and dried under vacuum at 50°C . The results of the radical copolymerization of *p*-DBMI (M_1) with St (M_2) were summarized in **Table 1**.

It can be seen that the initial rate (R_p) decreases as mole percentage of *p*-DBMI in the feed is increased. There is no maximum rate at around the equimolar feed as might be expected if the copolymerisation simply involved propagation *via* the homopolymerization of a charge-transfer complex. The monomer reactivity ratios r_1 and r_2 and the Q_1 and e_1 values for the *p*-DBMI(M_1)-St(M_2) system were obtained as follows: $r_1=0.01306$, $r_2=0.01385$, $Q_1=7.05$, $e_1=2.13$. The abnormal Q_1 values could be explained by the formation of molecular complex in the transition state between *p*-DBMI and St.

Table 1. Copolymerization of *p*-DBMI (M_1) and St (M_2) in Dioxane at 65 °C with AIBN as Initiator (Polymerization Times 2-5h)^a

f_1	R_p^b (mol/L \times S ⁻¹)	F_1^c	\bar{M}_n (g/mol)	\bar{M}_w / \bar{M}_n	T_g^e (°C)	T_i^f (°C)	
						In N ₂	In air
0.20	4.8×10^{-6}	0.4874	32830	4.56	166.0	398	365
0.40	3.5×10^{-6}	0.4978	20368	4.33	167.0	394	370
0.50	2.7×10^{-6}	0.4989	13878	3.45	168.0	390	365
0.60	2.0×10^{-6}	0.5054	7884	3.63	169.2	387	367
0.80	4.6×10^{-7}	0.5120	1837	4.55	170.0	361	348

^a $[M_1+M_2]=1.00$ mole/L, $[AIBN]=4 \times 10^{-3}$ mole/L. ^b By weight. ^c By ¹H-NMR in CDCl₃. ^d By GPC in THF. ^e By DSC at a heating rate 10 °C/min in N₂. ^f Temperature at which initial weight loss was recorded by TG at a heating rate 20 °C/min.

The resulting copolymers were colorless powders and highly soluble in chloroform, acetone, *etc.* The number-average molecular weights of these copolymers distribute in the range of $1.837-32.830 \times 10^3$ g/mole with the polydispersity from 3.45 to 4.56, and decrease sharply with increasing mole percentage of *p*-DBMI in monomer feeds. The T_g 's of the copolymers were recorded in the range of 166-170 °C. The T_i 's of the copolymers varied in the range of 348-370 °C in air and 361-398 °C in nitrogen.

The copolymers were also characterized by spectroscopy and the typical results were shown in **Table 2**. The spectroscopy data obtained corresponded very well with the structure of the copolymer.

Table 2. The ¹H-NMR, IR, and UV Data of the Typical Copolymer ($F_1=0.4989$)

Units of structure	¹ H-NMR ^a (ppm)	IR (cm ⁻¹)	UV (nm)
<i>p</i> -DBMI	2.5-4.5 (-CH-, m)		
	6.78 (=CH-, s, 1H)		
	7.55 (Ar-H, s, 5H)	1600-1560 (enol form)	250 (C=O)
	7.94 (Ar-H, s, 4H)	3400 (-O-H...)	
	16.80 (-OH...O, s, 0.9H)	1777, 1380, 780 (Imide ring) 1186 (C-N-C succinimide)	340 (enol form)
St	1.8-2.5 (-CH-, -CH ₂ -, m)	702, 759, 1600, 3100 (Bz)	
	7.18 (Bz-H, s, 5H)	2956 (-CH-, -CH ₂ -,)	

^am: multiplet, s: single.

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