

Copolymerization Reactivity Ratios of *p*-Vinylbenzophenone and *p*-Dimethylamino Styrene

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Polymers carrying benzophenone (electron acceptor) and dimethyl-aminophenyl (electron donor) side groups undergo easily photocrosslinking. Such polymers are easily obtained by copolymerization of *p*-vinylbenzophenone (VB) and *p*-dimethylaminostyrene (DAS). Their photocrosslinking, which requires the formation of EDA complexes in their photoexcited state, depends evidently on the composition and the internal structure of the copolymers and occasionally of the terpolymers, when the monomers are separated from each other by incorporation of an inert third monomer as methyl acrylate. In such systems crossed dyad concentration (donor-acceptor pairs) and monomer sequence distribution can only be evaluated on the basis of the copolymerization reactivity ratios.¹

In the present communication we wish to report copolymerization data for four systems which have been used in recent investigations^{2,3} namely *p*-vinylbenzophenone (VB), *p*-dimethylaminostyrene (DAS), VB-methyl acrylate (MA), VB-*p*-dimethyl-aminomethylstyrene (DMAS), and DAS-methyl acrylate. To our knowledge these values were not mentioned previously in the literature.

Radical copolymerizations of VB-DAS, VB-DMAS, VB-MA, and DAS-MA were carried out in benzene solution at 65°C in the presence of 0.01 mol L⁻¹ of azobisisobutyronitrile. The total monomer concentration was kept constant at 2 mol L⁻¹. After reaction and dilution the copolymers were precipitated in methanol (except when indicated H for *n*-hexane), redissolved, and precipitated again.

The composition of the copolymers was determined by ¹H NMR spectroscopy, and also by nitrogen elemental analysis for the VB-DAS and VB-DMAS pairs. The results of both methods agree satisfactorily (see Table II). The data are summarized in Tables I-IV.

The reactivity ratios have been determined according to the method of Fineman and Ross.⁴ The copolymerization diagrams are given in Figures 1 and 2, where the curves correspond to the compositions calculated on the basis of the indicated *r* values. The copolymerization reactivity ratios are summarized in Table V.

On the basis of these values, crossed dyad probabilities P_{12} can be calculated, e.g., $P_{12} = 0.43$ for a co(VB 77-DAS 23) polymer. The great differences between the two first pairs should be stressed; their alternating tendencies, as measured by the reciprocals of $r_1 r_2$ are, respectively, 32 and 1.7. The influence of the internal structure of the polymeres on their absorption and emission spectral behavior as well as on their photolysis in benzene solution has been described previously.^{2,3}

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TABLE I
Radical Copolymerization of *p*-vinylbenzophenone and *p*-dimethylaminostyrene

VB mol %	Polym. time/min.	conversion wt %	Copolymer Nitrogen (wt %)	VB mole %
80	30	10.5	1.42	80
			1.40	
60	35	10.3	2.30	69
			2.28	
50	35	10.5	2.75	64
			2.66	
40	40	9.9	3.15	59
			3.14	
20	60	8.6	4.43	45
			4.41	

TABLE II
Radical Copolymerization of *p*-Vinylbenzophenone and *p*-Dimethylaminomethylstyrene

VB mol %	Polym. time/min.	Conversion wt. %	Copolymer Nitrogen wt. %	VB mole %
90	30	8.9	0.28	96(95) ^c
			0.29	
80	30	7.3	0.59	91(89)
			0.56	
70	30	7.0(H) ^a	1.02	86(85)
			0.98	
60	35	9.3(H)	1.50	79(77)
			1.46	
50	40	8.1(H)	2.04	72(71)
			1.99	
40	40	7.9(H)	2.65	64(62)
			2.62	
30	50	8.2(H)	3.41	55(53)
			3.37	
20	55	5.7(H)	4.29	45(44)
			4.25	
10	70	5.7 ^b	5.77	28(27)
			5.77	

^a H indicates precipitation in *n*-hexane.

^b Isolated after freeze-drying benzene solution.

^c Values between parentheses are VB mole % as determined by ¹H NMR.

TABLE III
Radical Copolymerization of *p*-vinylbenzophenone and Methyl Acrylate

VB mol %	Polym. time/min.	Conversion wt. %	Copolymer VB in mole %
4	90	13	22
8	60	5	37
20	50	3	59
40	40	3	77
60	30	3	84

TABLE IV
Radical Copolymerization of *p*-Dimethylaminostyrene and Methyl Acrylate

DAS mole %	Polym. time/min.	Conversion wt. %	Mole % DAS in copolymer
3	60	14	19
6	60	13	32
12	60	11	37
21	90	6	48
40	75	6	54
60	60	3	63
75	120	5	67
85	120	4	72

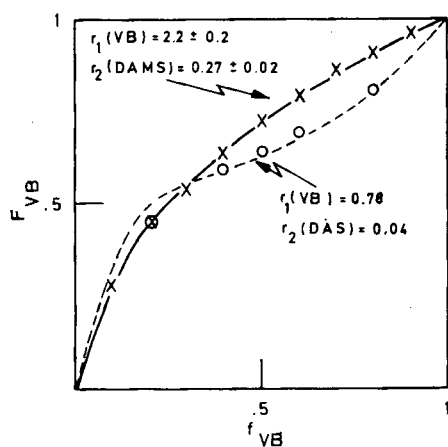


Fig. 1. Copolymer composition (mole fraction F_{VB}) as a function of monomer composition (mole fraction f_{VB}) for VB-DAS and VB-DAMS systems.

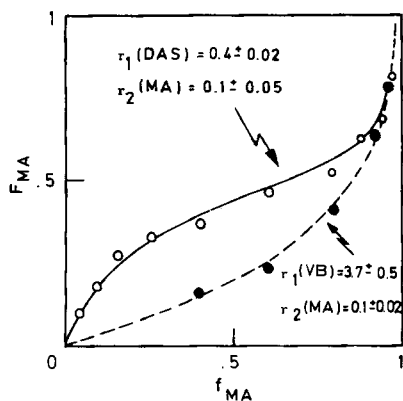


Fig. 2. Copolymer composition (mole fraction F_{MA}) as a function of monomer composition (mole fraction f_{MA}) for DAS-MA and VB-MA systems.

TABLE V
Copolymerization Reactivity Ratios

M ₁	M ₂	r ₁	r ₂
p-vinylbenzophenone	p-Me ₂ N-styrene	.78	.04
" " "	p-Me ₂ NCH ₂ -styrene	2.2 ± 0.2	.27 ± .02
" " "	methyl acrylate	3.7	.1
p-Me ₂ N-styrene	methyl acrylate	.4	.1

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References

1. F. A. Bovey, *Chain Structure and Conformation of Macromolecules*, Academic, New York, 1982, p. 137 and further.
2. G. Smets, S. N. El Hamouly, and T. J. Oh, *Pure Appl. Chem.*, **56** 439 (1984).
3. G. Smets, *Polym. J.*, **17**, 153 (1985).
4. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

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