Copolymerizations of *N*-Vinylsuccinimide and of *N,N*-Methyl Vinyl *p*-Toluenesulfonamide with Some Vinyl Compounds

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INTRODUCTION

N-Vinylsuccinimide is known to be readily polymerized by a radical mechanism.[1] but there have been few works available on the copolymerization reactions of *N*-vinylsuccinimide with other monomers. The polymerizability of *N,N*-methyl vinyl *p*-toluenesulfonamide is also unknown.

This study has been undertaken to examine the behavior of *N*-vinylimide and *N*-vinylsulfonamide in copolymerization with other vinyl monomers and to obtain information on the correlation between reactivity and structure in the unsaturated imide and amide.
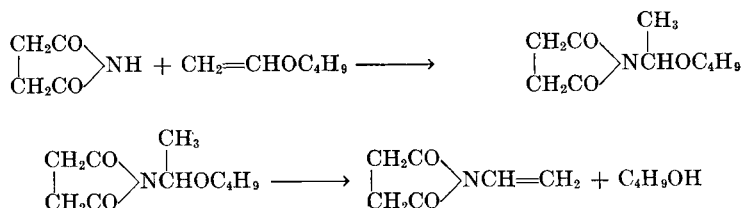
EXPERIMENTAL

Materials

N-Vinylsuccinimide* was recrystallized twice from ether, washed with petroleum ether, and dried *in vacuo* at 34°C.: colorless plates, m.p. 48–49°.

N,N-Methyl vinyl *p*-toluenesulfonamide* was recrystallized twice from benzene-petroleum ether mixture and dried *in vacuo* at 34°C.: colorless plates, m.p. 56.0–57.7°.

* *N*-Vinylsuccinimide was prepared by the following method:

$$\underset{\text{CH}_2\text{CO}}{\overset{\text{CH}_2\text{CO}}{\Big\rangle}}\text{NH} + \text{CH}_2\text{=CHOC}_4\text{H}_9 \longrightarrow \underset{\text{CH}_2\text{CO}}{\overset{\text{CH}_2\text{CO}}{\Big\rangle}}\text{NCHOC}_4\text{H}_9 \;(\text{CH}_3)$$

$$\underset{\text{CH}_2\text{CO}}{\overset{\text{CH}_2\text{CO}}{\Big\rangle}}\text{NCHOC}_4\text{H}_9\;(\text{CH}_3) \longrightarrow \underset{\text{CH}_2\text{CO}}{\overset{\text{CH}_2\text{CO}}{\Big\rangle}}\text{NCH=CH}_2 + \text{C}_4\text{H}_9\text{OH}$$

N,N-Methyl vinyl *p*-toluenesulfonamide was prepared in a similar way [J. Furukawa, A. Onishi, and T. Tsuruta, *J. Org. Chem.*, **23**, 672 (1958)].

Vinyl acetate was washed successively with a saturated solution of sodium bisulfite and water, and was distilled four times.   A fraction of b.p. 72° was redistilled in the presence of benzoyl peroxide immediately before use.

Methyl acrylate was steam-distilled twice, dried with sodium sulfate for 24 hr., and then with calcium chloride for a while, and was redistilled: b.p. 79.5–80.6°.

Methyl methacrylate was purified in a similar way.

The other monomers and reagents were purified by standard methods.[2]

TABLE I

Copolymerization of N-Vinylsuccinimide with Vinyl Acetate (60°C.)*

No.	Polymerization time, min.	Conversion, %	N content of copolymers, %	Remaining monomers VSI, mole × 10³	VAc, mole × 10³
A1-1	0	0	—	2.83	40.3
2	60	10.37	3.84	1.73	37.2
3	90	15.88	3.41	1.33	35.3
4	120	19.13	3.09	1.19	34.0
5	150	21.09	3.05	1.05	33.3
A2-1	0	0	—	5.38	37.3
2	30	4.21	6.77	4.59	36.6
3	60	15.02	5.72	2.99	34.0
4	90	21.18	4.85	2.53	31.9
5	120	28.59	4.57	1.75	29.7
6	150	38.37	4.11	1.01	26.4
7	180	47.58	3.60	0.62	22.8
A3-1	0	0	—	9.63	32.7
2	10	1.27	7.91	9.34	32.5
3	20	5.13	7.88	8.48	32.0
4	40	12.27	7.78	6.89	31.0
5	50	14.86	7.32	6.51	30.3
6	15	1.19	8.32	9.35	32.5
7	30	4.28	8.46	8.60	32.2
8	45	10.33	7.91	7.29	31.3
9	60	14.58	7.49	6.52	30.4
10	75	18.97	7.52	5.54	29.0
A4-1	0	0	—	13.2	28.7
2	30	11.64	8.37	10.3	27.3
3	40	17.66	8.61	8.70	26.8
4	50	24.37	8.26	7.25	25.7
A5-1	0	0	—	16.9	24.5
2	10	2.39	9.64	16.2	24.3
3	30	22.54	9.19	10.6	22.5
A6-1	0	0	—	20.6	19.9
2	4	0.74	10.2	20.3	19.9
3	8	1.86	10.1	20.0	19.8
4	20	10.69	9.84	17.3	19.3
5	24	13.58	9.67	16.5	19.0

* Monomer ratio, VAc:VSI (by weight), in feed: A1 (9:1); A2, (8:2); A3, (7:3); A4, (6:4); A5, (5:5); A6, (4:6).

TABLE II
Copolymerization of *N*-Vinylsuccinimide with Acrylonitrile (60°C.)

No.	In comonomer			BPO concn., mole-%	Polymerization time, min.	Conversion, %	In copolymer	
	VSI, g.	AN, g.	Molar ratio, VSI:AN				N content, %	Molar ratio, VSI:AN
N1-1	3.42	0.90	9:1	0.01	30	1.2	23.21	9.0:1.0
2	"	"	"	"	60	4.1	23.07	8.9:1.1
N2-1	2.88	1.69	8:2	"	30	1.5	20.02	7.6:2.4
2	"	"	"	"	45	1.5	20.27	7.8:2.2
3	"	"	"	"	60	3.1	20.14	7.7:2.3
4	"	"	"	"	90	11.1	19.98	—
5	"	"	"	"	120	9.6	18.55	—
N3-1	2.40	2.42	7:3	"	30	1.6	18.32	6.7:3.3
2	"	"	"	"	50	5.6	19.51	7.4:2.6
3	"	"	"	"	70	7.3	18.79	7.0:3.0
N4-1	1.90	3.16	6:4	"	30	4.1	17.47	6.2:3.8
2	"	"	"	"	50	8.6	17.53	6.3:3.7
N5-1	1.54	3.64	5:5	"	25	2.4	16.55	5.7:4.3
2	"	"	"	"	40	7.9	16.31	5.4:4.6
3	"	"	"	"	55	10.3	16.54	5.6:4.4
N6-1	1.60	5.63	4:6	"	15	1.6	16.00	5.2:4.8
2	"	"	"	"	25	3.0	16.01	5.2:4.8
3	"	"	"	"	35	6.4	16.15	5.3:4.7
N7-1	0.80	4.38	3:7	"	30	1.4	15.97	5.2:4.8
2	"	"	"	"	40	3.1	16.10	5.3:4.7
3	"	"	"	"	50	2.1	16.02	5.2:4.8
N8-1	0.40	3.75	2:8	"	30	2.9	14.78	4.2:5.8
2	"	"	"	"	40	5.7	14.15	4.0:6.0
3	"	"	"	"	50	7.0	14.75	4.2:5.8
N9-1	0.40	8.47	1:9	0.005	60	3.0	12.70	2.1:7.9

TABLE III

Copolymerization of N-Vinylsuccinimide with Styrene (60°C.)

No.	In comonomer			BPO concn., mole-%	Polymerization time, min.	Conversion, %	In copolymer	
	VSI, g.	St, g.	Molar ratio, VSI:St				N content, %	Molar ratio, VSI:St
S1-1	3.00	0.75	8.3:1.7	0.02	255	1.8	—	—
2	"	"	"	"	345	2.5	—	—
3	"	"	"	"	415	3.0	—	—
S2-1	2.40	1.60	6.4:3.6	"	155	1.0	0.92	9.3:0.7
2	"	"	"	"	285	1.7	0.96	9.3:0.7
3	"	"	"	"	355	2.1	—	—
S3-1	2.05	2.05	5.5:4.5	"	195	0.6	1.52	8.5:1.5
2	"	"	"	"	375	2.0	—	—
S4-1	1.70	2.55	4.6:5.4	"	250	0.9	2.25	8.2:1.8
2	"	"	"	"	380	1.3	—	—
S5-1	1.80	3.24	4:6	1.0	370	11.8	2.46	8.1:1.9
2	"	"	"	"	400	13.4	2.53	8.0:2.0
3	"	"	"	"	430	13.7	2.36	8.2:1.8
S6-1	1.35	3.78	3:7	"	370	11.2	2.98	7.7:2.3
2	"	"	"	"	400	13.5	2.96	7.7:2.3
3	"	"	"	"	430	12.1	2.98	7.7:2.3
S7-1	0.90	4.32	2:8	"	350	9.5	3.81	7.0:3.0
2	"	"	"	"	380	13.3	4.66	6.3:3.7
3	"	"	"	"	410	13.5	4.69	6.3:3.7
S8-1	0.45	4.86	1:9	"	350	18.6	7.31	4.1:5.9
2	"	"	"	"	380	27.4	8.10	3.1:6.9

TABLE IV

Copolymerization of N-Vinylsuccinimide with Methyl Acrylate (60°C.)

| | In comonomer | | | | | | In copolymer | |
No.	VSI, g.	MA, g.	Molar ratio, VSI:MA	BPO concn., mole-%	Polymerization time, min.	Conversion, %	N content, %	Molar ratio, VSI:MA
M1-1	3.43	0.39	9.3:0.7	0.01	45	4.5	1.69	9.0:1.0
M2-1	3.14	0.79	8.5:1.5	0.005	65	4.8	2.32	8.5:1.5
2	"	"	"	"	75	6.9	2.15	8.6:1.4
M3-1	2.78	1.21	7.7:2.3	"	80	18.5	2.94	8.0:2.0
2	"	"	"	"	100	36.5	2.81	8.1:1.9
M4-1	2.44	1.64	6.8:3.2	"	75	2.0	3.91	7.2:2.8
2	"	"	"	"	90	3.2	3.69	7.5:2.5
M5-1	2.07	2.10	5.9:4.1	"	45	0.3	4.66	6.7:3.3
2	"	"	"	"	75	3.3	5.13	6.4:3.7
3	"	"	"	"	90	6.4	4.08	7.2:2.8
M6-1	1.86	2.86	4.9:5.1	"	50	3.3	6.22	5.3:4.7
M7-1	0.93	3.82	3.7:6.3	"	60	19.8	6.62	5.0:5.0
M8-1	0.47	4.29	1.3:8.7	"	40	3.3	9.70	2.5:7.5

TABLE V. Copolymerization of N-Vinylsuccinimide with n-Butyl Vinyl Ether (60°C.)

No.	In comonomer				Polymerization time, min.	Conversion, %	In copolymer	
	VSI, g.	BVE, g.	Molar ratio VSI:BVE	BPO concn., mole-%			N content, %	Molar ratio VSI:BVE
E1-1	3.87	0.54	9:1	1.0	55	5.8	9.41	1.9:8.1
2	"	"	"	"	120	6.5	9.11	2.2:7.8
3	"	"	"	"	450	6.9	9.37	2.0:8.0
E2-1	"	1.21	8:2	"	30	9.3	10.05	1.2:8.8
2	"	"	"	"	45	15.6	9.92	1.4:8.6
3	"	"	"	"	75	17.3	9.48	1.9:8.1
E3-1	"	2.07	7:3	"	20	16.2	9.92	1.4:8.6
2	"	"	"	"	35	23.6	9.90	1.4:8.6
3	"	"	"	"	45	26.1	—	—
E4-1	1.56	1.29	6:4	0.2	35	5.2	10.42	0.9:9.1
2	"	"	"	"	60	6.5	10.61	0.6:9.4
3	"	"	"	"	90	6.1	10.43	0.8:9.2
E5-1	"	1.94	5:5	"	30	2.2	10.82	0.4:9.6
2	"	"	"	"	60	6.6	10.73	0.5:9.5
3	"	"	"	"	90	6.2	10.65	0.6:9.4
E6-1	"	2.92	4:6	"	30	7.0	10.80	0.4:9.6
2	"	"	"	"	60	7.2	10.94	0.3:9.7
3	"	"	"	"	90	8.1	10.69	0.6:9.4
E7-1	0.77	2.26	3:7	0.1	30	5.4	10.32	1.0:9.0
2	"	"	"	"	60	5.9	10.53	0.7:9.3
3	"	"	"	"	90	6.1	10.47	0.8:9.2
E8-1	0.77	3.89	2:8	0.07	30	0.3	11.51	—
2	"	"	"	"	90	1.1	10.82	0.4:9.6
3	"	"	"	"	210	0.3	10.23	1.1:8.9
E9-1	0.39	4.35	1:9	0.1	30	12.4	10.84	0.4:9.6
2	"	"	"	"	45	9.9	10.64	0.6:9.4
3	"	"	"	"	60	11.9	10.74	0.5:9.5

Procedure

A mixture of a monomer pair and catalyst was placed in a test tube of 20–30 ml. capacity. The air in the tube was displaced by flushing with nitrogen. The sealed tube was rotated (30–35 r.p.m.) in a thermostat, the temperature of which was controlled to 60.0 ± 0.1°C. The polymerization proceeded in a homogeneous phase except for the case of acrylonitrile and *n*-butyl vinyl ether as co-monomer. After a definite time interval, the polymerization was interrupted by adding a small quantity of hydroquinone. The copolymer was precipitated from the solution by adding an appropriate nonsolvent, steam distilled to remove the monomers and solvents, and dried for several hours at 50–70°C. The composition of the polymer was determined by the nitrogen analysis.

RESULTS AND DISCUSSION

The results of the copolymerization of *N*-vinylsuccinimide (VSI) with vinyl acetate (VAc), acrylonitrile (AN), styrene (St), methyl acrylate (MA) and *n*-butyl vinyl ether (BVE) are shown in Tables I–V.

The overall rate of copolymerization of *N*-vinylimide with styrene was smaller than the rates of copolymerization with vinyl acetate, acrylonitrile, and methyl acrylate, but larger than that with *n*-butyl vinyl ether as comonomer. The monomer reactivity ratios were calculated according to the Mayo-Lewis formulas.[3] From the reactivity ratios of the five pairs of the monomers, the values for Q and e of *N*-vinylsuccinimide[4] were obtained. These are shown in Table VI.

TABLE VI
Monomer Reactivity Ratios and Factors of *N*-Vinylsuccinimide

Monomer (2)	r_1	Q_1	e_1	r_2	Q_2	e_2
n-Butyl vinyl ether	15	0.16	-0.26^a	0	0.015	-1.6
Styrene	0.09	0.10	-0.12	7.0	1.0	-0.8
Vinyl acetate	6.05	0.12	-0.3	0.18_5	0.022	-0.3
Methyl acrylate	0.4	0.21	-0.25	1.2	0.42	0.6
Acrylonitrile	0.16	0.12	-0.37	0.54	1.2	0.44
	mean	0.15	-0.26			

^{a} This value was assumed from the mean.

N,N-Methyl vinyl *p*-toluenesulfonamide, unlike *N*-vinylsuccinimide, has been found[5] not to be polymerized under the action of benzoyl peroxide,* while the radical copolymerization of the *N*-vinylsulfonamide with some monomers was possible. In every case, however, an increase in the mole ratio of the *N*-vinylsulfonamide in the monomer mixture considerably lowered the copolymer yield.

* On the other hand, a cationic polymerization of *N,N*-methyl vinyl *p*-toluenesulfonamide is induced by boron trifluoride.

TABLE VII

Copolymerization of N,N-Methyl Vinyl p-Toluenesulfonamide with Acrylonitrile (60°C.)

No.	In comonomer			BPO concn., mole-%	ABN concn., mole-%	Polymerization time, min.	Conversion, %	In copolymer	
	VSA, g.	AN, g.	Molar ratio, VSA:AN					N content, %	Molar ratio, VSA:AN
N1-1	0.713	1.612	1:9	1.0		20	12.3	17.62	1.67:8.33
2	"	"	"	"		35	16.2	17.19	1.80:8.20
3^a	0.321	0.725	"		0.5	450	53.7	16.27	2.09:7.91
4	"	"	"		"	55	11.3	17.77	1.62:8.38
5	"	"	"		"	30	10	17.82	1.61:8.39
N2-1	0.802	0.806	2:8	1.0		15	8.4	14.41	2.78:7.22
2	"	"	"	"		30	9.8	14.36	2.81:7.19
3	0.642	0.645	"		0.5	450	10.2	15.69	2.29:7.71
4	"	"	"		"	65	8.7	14.22	2.86:7.14
N3-1	0.963	0.564	3:7		"	100	8.0	14.13	2.91:7.09
2	"	"	"		"	90	10	13.14	3.38:6.62
3	"	"	"		"	180	"	13.23	3.33:6.67
N4-1	1.283	0.483	4:6		0.75	270	"	12.31	3.83:6.17

^{a} Conversion is so large that this value is not taken into calculation of monomer reactivity ratios.

TABLE VIII

Copolymerization of *N,N*-Methyl Vinyl *p*-Toluenesulfonamide with Methyl Methacrylate (60°C.)

No.	In comonomer			BPO concn., mole-%	ABN concn., mole-%	Polymeri- zation time, min.	Con- ver- sion, %	In copolymer	
	VSA, g.	MMA, g.	Molar ratio, VSA:MMA					N content, %	Molar ratio, VSA:MMA
M1-1	0.198	0.842	1:9	1.0		30	6.7	0.45	0.33:9.67
2	"	"	"	"		35	7.5	0.47	0.35:9.65
3	"	"	"	"		30	5.1	0.58	0.43:9.57
4	"	"	"	"		"	5.6	0.62	0.47:9.53
5	"	"	"	"		"	5.3	0.68	0.51:9.49
M2-1	0.395	0.749	2:8		2.0	60	17.1	0.46	0.34:9.66
2	"	"	"	1.0		"	19.6	0.82	0.63:9.47
3	"	"	"	"		20	2.6	0.80	0.61:9.39
4	"	"	"	"		80	10.9	1.04	0.81:9.19
5	"	"	"	"		40	6.0	0.68	0.51:9.49
6	"	"	"	"		"	7.1	0.56	0.42:9.58
7	"	"	"	"		50	11.9	0.93	0.72:9.28
8	"	"	"	"		"	10.0	0.83	0.63:9.37
M3-1	0.593	0.655	3:7	"		40	2.2	0.48	0.36:9.64
2	"	"	"	"		80	2.2	0.50	0.37:9.63
3	"	"	"	"		120	5.7	0.66	0.50:9.50
4	"	"	"	"		80	9.7	0.85	0.65:9.35
5	"	"	"	"		"	9.1	0.93	0.72:9.28

TABLE IX

Copolymerization of N,N-Methyl Vinyl p-Toluenesulfonamide with Styrene (60°C.)

No.	In comonomer			BPO concn., mole-%	Polymerization time, min.	Conversion, %	In copolymer	
	VSA, g.	St, g.	Molar ratio, VSA:St				N content, %	Molar ratio, VSA:St
S1-1[a]	0.183	0.811	1:9	5.0	360	42.7	0.92	0.74:9.26
2	"	"	"	3.9	40	5.0	0.30	0.23:9.77
3	"	"	"	"	50	5.8	0.32	0.24:9.76
4	"	"	"	"	60	6.6	0.28	0.21:9.79
S2-1[a]	0.366	0.721	2:8	5.0	360	41.2	0.78	0.61:9.39
2	"	"	"	3.4	70	6.0	0.42	0.32:9.68
3	"	"	"	"	90	7.6	0.45	0.35:9.65
4	"	"	"	"	115	9.3	0.31	0.24:9.76
S3-1	0.549	0.631	3:7	3.0	130	8.8	0.45	0.35:9.65
2	"	"	"	"	140	6.8	0.37	0.28:9.72
3	"	"	"	"	160	10.1	0.38	0.29:9.71
S4-1	0.731	0.541	4:6	5.0	60	4.7	0.73	0.57:9.43
2	"	"	"	"	90	6.6	0.66	0.51:9.49
3	"	"	"	"	120	9.7	0.58	0.45:9.55
S5-1	0.731	0.541	5:5	5.0	150	7.8	0.86	0.68:9.32
2	"	"	"	"	180	10.0	0.79	0.62:9.38
3	"	"	"	"	210	9.2	0.89	0.70:9.30
S6-1	1.097	0.360	6:4	5.0	240	9.2	0.99	0.79:9.21
2	"	"	"	"	270	9.9	1.01	0.81:9.19
3	"	"	"	"	300	11.3	0.98	0.78:9.22

[a] Conversions are so large that these values are not taken into calculation of monomer reactivity ratios.

In Tables VII, VIII, and IX are summarized the results of the copolymerization of *N,N*-methyl vinyl *p*-toluenesulfonamide with acrylonitrile, methyl methacrylate, and styrene. Mixtures of the *N*-vinylsulfonamide and either of methyl acrylate or vinyl acetate were found not to give copolymers under the experimental condition.

The monomer reactivity ratios calculated according to the Mayo-Lewis formula[3] are listed in Table X. Since *N,N*-methyl vinyl *p*-toluenesulfonamide is incapable of homopolymerizing by radical initiators, we assumed its reactivity ratio, r_1, equal to zero. The r_2 values obtained may involve considerable errors because these values were based upon the extremely small differences in the % N of the copolymers. In Table XI, Q and e values[4] of the *N*-vinylsulfonamide are also tabulated.

It can be seen from the results obtained that *N*-vinylsuccinimide has the larger copolymerizability compared with *N,N*-methyl vinyl *p*-toluenesulfonamide.

TABLE X
Monomer Reactivity Ratios of *N,N*-Methyl Vinyl *p*-Toluenesulfonamide (60°C.)

Monomer (2)	r_1	r_2
Acrylonitrile	0	0.42
Methyl methacrylate	0	4.68
Styrene	0	12.3

TABLE XI
Monomer Reactivity Factors of *N,N*-Methyl Vinyl *p*-Toluenesulfonamide (60°C.)

Pair of comonomer	Q	e
(VSA-AN)–(VSA-St)	0.086	−0.88
(VSA-AN)–(VSA-MMA)	0.098	−0.77
(VSA-St)–(VSA-MMA)	0.092	−0.96
mean	0.092	−0.87

The Q value ($=0.10$–0.21) of *N*-vinylsuccinimide is much larger than those of vinyl acetate ($=0.022$) and alkyl vinyl ether ($=0.015$).[6] Partial accounting for this larger copolymerizability of the *N*-vinylimide may be the conjugation between vinyl and carbonyl groups through the nitrogen atom. (We consider that the electron structure of the N atom in *N*-vinylsuccinimide is probably sp^2 as in the case of aniline molecule in which the $2p_\pi$ electrons of the N atom are in the conjugated system involving the aromatic π-orbital.) The electron attracting character of the carbonyl groups may contribute to the reactivity by shifting the polarity of the monomer to the more positive side which favors the homopolymerization.

On the other hand, in *N,N*-methyl vinyl *p*-toluenesulfonamide, the contribution of 3*d*-orbital of sulfur atom to the conjugated system does not seem so large. The Q values of methyl vinyl ketone and of methyl

vinyl sulfone are reported as 1.0^{6a} and $0.11,^8$ respectively. $N.N$-Methyl vinyl benzamide, the carbonyl derivative corresponding to N,N-methyl vinyl p-toluenesulfonamide, is known to be polymerized by a radical mechanism with azobisisobutyronitrile as initiator.[7] These observations suggest that the degree of incorporation of the sulfone group in the conjugated system is smaller than that of the carbonyl group, but the relatively small difference in Q for the present two monomers (N-vinylsuccinimide and N,N-methyl vinyl p-toluenesulfonamide) may suggest that the greater ease of homopolymerization of N-vinylsuccinimide may be because its e value is closer to zero, thus giving less electrical repulsion in homopolymerization.

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Synopsis

The copolymerizations of N-vinylsuccinimide (VSI) and of N,N-methyl vinyl p-toluenesulfonamide (VSA) with vinyl acetate (VAc), acrylonitrile (AN), styrene (St), methyl acrylate (MA), methyl methacrylate (MMA), and n-butyl vinyl ether (BVE) were examined at 60°C., using benzoyl peroxide or azobisisobutyronitrile as initiator. The monomer reactivity ratios and the monomer reactivity factors of VSI and VSA were as follows. VSI as monomer 1: $r_1 = 15$, $r_2 = 0$ (VBE); $r_1 = 0.09$, $r_2 = 7.0$ (St); $r_1 = 6.05$, $r_2 = 0.185$ (VAc); $r_1 = 0.4$, $r_2 = 1.2$ (MA); $r_1 = 0.16$, $r_2 = 0.54$ (AN); $Q_1 = 0.15$, $e_1 = -0.26$. VSA as monomer 1: $r_1 = 0$, $r_2 = 0.42$ (AN); $r_1 = 0$, $r_2 = 4.68$ (MMA) $r_1 = 0$, $r_2 = 12.3$ (St); $Q_1 = 0.092$, $e_2 = -0.87$. The difference in copolymerizability between VSI and VSA seems to arise primarily from the difference in their polarity factors.

Résumé

On a étudié la copolymérisation de la N-vinylsuccinimide (VSI) et de la N,N-méthyl vinyl p-toluènesulfonamide (VSA) avec l'acétate de vinyle (VAc), l'acrylonitrile (AN), le styrène (St), l'acrylate de méthyle (MA), le méthacrylate de méthyle (MMA) et l'éther de N-butyl-vinylique (BVE) à 60°C, le peroxyde de benzoyle et l'azoisobutyronitrile servant d'initiateurs. Les constantes de copolymérisation et les facteurs de réactivité du monomère ont les valeurs suivants pour VSI et VSA. Si l'on emploie VSI comme premier monomère, on obtient: $r_1 = 15$, $r_2 = 0$ (VBE); $r_1 = 0,09$, $r_2 = 7,0$ (St); $r_1 = 6,05$, $r_2 = 0,185$ (VAc); $r_1 = 0,4$, $r_2 = 1,2$ (MA); $r_1 = 0,16$, $r_2 = 0,54$ (AN); $Q_1 = 0,15$, $e_1 = -0,26$. Si l'on emploie maintenant VSA comme premier monomère, on obtient cette fois: $r_1 = 0$, $r_2 = 0,42$ (AN); $r_1 = 0$, $r_2 = 4,68$ (MMA); $r_1 = 0$, $r_2 = 12,3$

(St); $Q_1 = 0,092$, $e_1 = -0,87$. Le comportement différent de VSI et VSA à la copolymérisation semble provenir en premier lieu de la différence de leur facteur de polarité.

Zusammenfassung

Die Copolymerisation von *N*-Vinylsuccinimid (VSI) und von *N*,*N*-Methylvinyl-*p*-toluolsulfonamid (VSA) mit Vinylacetat (VAc), Acrylnitril (AN), Styrol (St), Methylacrylat (MA), Methylmethacrylat (MMA) und *n*-Butylvinyläther (BVÄ) wurde bei 60°C mit Anregung durch Benzoylperoxyd oder Azo-bis-isobutyronitril untersucht. Folgende Copolymerisationsparameter wurden für VSI und VSA erhalten. VSI als Monomeres 1: $r_1 = 15$, $r_2 = 0$ (VBE); $r_1 = 0,09$, $r_2 = 7,0$ (St); $r_1 = 6,05$, $r_2 = 0,185$ (VAc); $r_1 = 0,4$, $r_2 = 1,2$ (MA); $r_1 = 0,16$, $r_2 = 0,54$ (AN); $Q_1 = 0,15$, $e_1 = -0,26$. VSA als Monomeres 1: $r_1 = 0$, $r_2 = 0,42$ (AN); $r_1 = 0$, $r_2 = 4,68$ (MMA); $r_1 = 0$, $r_2 = 12,3$ (St); $Q_1 = 0,092$, $e_1 = -0,87$. Der Unterschied in der Copolymerisationsfähigkeit zwischen VSI und VSA scheint in erster Linie durch den Unterschied in ihren Polaritätsfaktoren bedingt zu sein.