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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Copolymers Based on Diallylhydrazines

A. I. Vorob'eva, M. N. Gorbunova, V. Yu. Gusev, R. R. Muslukhov, S. V. Kolesov, and A. G. Tolstikov

Institute of Technical Chemistry, Perm Scientific Center, Russian Academy of Sciences, Perm, Russia
Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, Bashkorkostan, Russia

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Abstract—The possibility of preparing polymers based on *N*,*N*-diallylhydrazine derivatives by allylation of carboxylic acid hydrazides was considered.

The range of nitrogen-containing allyl compounds from which linear macromolecular polymers can be produced by radical homo- and copolymerization is very limited. Actually, only quaternary diallylammonium salts are widely used as monomers for synthesis of polyfunctional polymers [1–3]. At the same time, such polymers exhibit unique properties [4–6], which makes it urgent to search for and study nitrogen-containing allyl monomers of new structural types. In this respect, promising monomers are *N*-allylated derivatives of carboxylic acid hydrazides. Hydrazides of aliphatic acids have flotation properties [7], and hydrazides of naphthenic acids are selective extracting agents for copper [8, 9].

Preparation of derivatives of *N*,*N*-diallylhydrazines (DAHs) is the way not only to produce new polyfunctional polymers but also to impart to them certain physicochemical and biological characteristics typical for the initial compounds. The first stage on this way is to establish the possibility of involving these derivatives in radical polymerization.

Here we attempted to prepare polymers based on DAHs, in particular, *N*,*N*-diallyl-*N*'-acylhydrazine (DAAH), *N*,*N*-diallyl-*N*'-propanoylhydrazine (DAPH), and *N*,*N*-diallyl-*N*'-benzoylhydrazine (DABH).

EXPERIMENTAL

N,*N*-Diallylhydrazines were synthesized by the reaction of hydrazides of aliphatic and aromatic acids with allyl halides (AllHlg):

$$\text{R–CO–NH–NH}_2 + 2\text{AllHlg} \rightarrow \text{R–CO–NH–N(All)}_2 + 2\text{HHlg},$$

where R is CH_3, C_3H_7, or C_6H_5.

The monomers used for the synthesis of copolymers were acrylonitrile (AN), acrylamide (AA), methyl methacrylate (MMA), vinyl acetate (VA), *N*-vinylpyrrolidone (VP); the initiators were azobis(isobutyronitrile) (AIBN), potassium persulfate (PP), and benzoyl peroxide (BP); the solvents were methanol, chloroform, and dimethyl sulfoxide. After purification by common procedures, the characteristics of all chemicals were in good agreement with published data. Sulfur dioxide was dried by passing through concentrated H_2SO_4 and freshly calcined $CaCl_2$.

Copolymerization of DAHs with vinyl monomers (VMs) was carried out in a vacuum in the bulk and in a solution in the presence of radical initiators (for polymerization conditions, see Table 1).

Copolymerization of DAHs with sulfur dioxide was carried out in a glass reactor by the procedure described in [10] (for polymerization conditions, see Table 2). The polymers were dried by twofold reprecipitation from a solvent to a precipitant chosen individually for each system. The purified polymers were dried in a vacuum at 50°C to constant weight. The compositions of copolymers were evaluated from the results of elemental analysis. The ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 75.46 MHz. DMSO-d_6 and D_2O were used as solvents, and tetramethylsilane and DSS, respectively, as internal references. The UV spectra were recorded on a Shimadzu UV-VIS-NIR 3100 spectrophotometer. The composition of the complex was determined by the method of isomolar series [11].

Under usual conditions, DAHs practically do not enter into homopolymerization by a free-radical mech-

Table 1. Copolymerization of diallylhydrazine derivatives (M_1) with VMs (M_2) [AIBN] = 3.0 wt %, *T* = 90°C

M_1	M_2	Composition of initial mixture, mol %		Medium	Yield, %	Copolymer composition, mol %		Solvent for copolymers
		M_1	M_2			m_1	m_2	
DAAH	MMA	50.0	50.0	In the bulk	31.5	18.3	81.7	DMSO, methanol, acetone, benzene, THF, chloroform
		66.6	33.4	″	12.8	23.0	73.0	
DAAH	AN	50.0	50.0	″	18.0	14.2	85.8	DMSO, DMF, pyridine
		57.9	42.1	″	12.8	25.0	75.0	
DAAH	AA	50.0	50.0	H_2O*	41.0	20.3	79.7	DMSO, H_2O
		64.4	35.6	Methanol	21.0	28.0	72.0	
DAAH	VA	50.0	50.0	In the bulk	11.0	38.0	62.0	DMSO, methanol, acetone
		65.7	34.3	″	3.0	–	–	
DAAH	VP	50.0	50.0	″	28.2	19.0	81.0	H_2O, methanol, acetone
		55.0	45.0	″	10.0	–	–	
DAAH	Acrylic acid	50	50	″	27.2	15.0	85.0	DMSO
DABH	AN	34	66	Methanol	29.3	10.2	89.8	DMSO, DMF, pyridine, acetone
DABH	AA	33	37	″	38.2	10.5	89.5	Insoluble

* Potassium persulfate initiator.

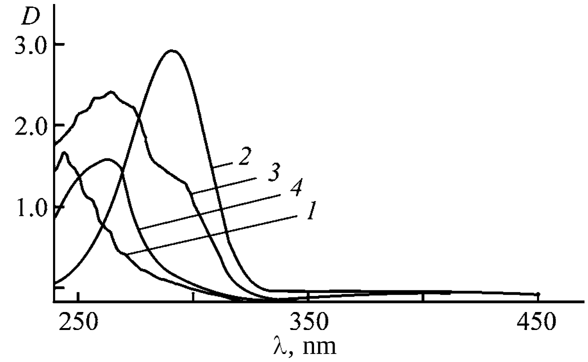
Table 2. Copolymerization of diallylhydrazine derivatives (M_1) with SO_2. Composition of the initial mixture: $M_1 : M_2 = 1 : 1$; [In] = 3.0 wt %, *T* = 90°C

M_1	Medium	Initiator	Yield, %	Copolymer composition, %		Solvent for copolymer
				m_1	m_2	
DAAH	In the bulk	AIBN	41.7	48.0	52.0	DMSO, water
		AIBN*	48.2	49.0	51.0	
	″	BP	5.6	47.0	53.0	
	Aqueous	PP	38.5	47.0	53.0	
	Acetone	AIBN	50.2	53.0	47.0	
	Chloroform	AIBN	60.0	48.0	52.0	
DAPH	In the bulk	AIBN	50.0	49.0	51.0	DMSO, methanol
	Chloroform	AIBN	70.4	48.0	52.0	
	Methanol	AIBN**	34.3	49.0	51.0	
	DMSO	AIBN**	44.4	50.0	50.0	
	Chloroform	AIBN**	57.4	48.0	52.0	
DABH	In the bulk	AIBN	23.1	49.0	51.0	DMSO, DMF
	Methanol	AIBN	35.5	50.0	50.0	

* In the presence of HCl.
** Polymerization duration 1 h.

anism. The activity of DAHs somewhat increases on adding protic and aprotic acids, which is a well-known procedure for activation of allyl monomers. However, in this case, e.g., in polymerization of DAAH in the presence of HCl, H_3PO_4, and $ZnCl_2$ at the ratio DAH : acid = 1 : 1.2 (*T* = 90°C, initiator AIBN, 30 h), the yield of the homopolymer did not exceed 6–10%.

The use of DAHs in radical copolymerization with VMs containing both electron-acceptor (AA, AN, and methacrylic acid) and electron-donor (VA and VP) substituents is significantly more efficient. Copolymerization of DAHs (M_1) with vinyl monomers (M_2) proceeds at a noticeable rate at a temperature above 80°C and initiator concentration of no less than 2.5 wt %. DAHs are less active than vinyl monomers.



Electronic absorption spectra of solutions in chloroform. (*D*) Optical density and (λ) wavelength. (*1*) DAAH ([DAAH] 1×10^{-1} M), (*2*) SO_2 ([SO_2] 1×10^{-3} M), (*3*) a mixture of DAAH and SO_2 ([DAAH] 5×10^{-3} M, [SO_2] 5×10^{-4} M), and (*4*) difference of spectrum *3* and half-sum of spectra *1* and *2*.

Copolymers of all the monomer pairs are enriched with VM units as compared to the composition of the initial mixture (Table 1). At the equimolar ratio of the monomers in the initial mixture, the content of DAHs in the copolymers (excluding the copolymer with VA) does not exceed 20 mol %.

In spite of high temperature (90°C) and high initiator concentration (3 wt %), the rate of copolymerization of DAHs with VM is low, especially at the content of M_1 in the reaction mixture exceeding 50 mol %.

DAHs are significantly more active in copolymerization with sulfur dioxide having high electron-acceptor power. All the DAHs copolymerize with SO_2 to form alternating copolymers with equimolar composition, irrespective of the ratio of the monomers in the initial mixture, solvent and initiator nature, and reaction temperature (Table 2). The constancy of the composition of the copolymers, irrespective of the ratio of the monomers in the reaction mixture, suggests that copolymerization of DAHs with SO_2 proceeds with formation of complexes [DAH$\cdots SO_2$]. The UV spectra of a mixture of DAAH with SO_2 in chloroform contain a new band of charge transfer with λ_{max} = 263 nm (for SO_2, λ_{max} = 275.9 nm), suggesting formation of a donor–acceptor complex (see figure).

The reaction conditions do not affect the composition of copolymers but significantly affect the copolymer yield (Table 2). In particular, higher yields of copolymers of DAH with SO_2 were obtained with AIBN and PP as an initiator; with BP, there was virtually no copolymerization.

In the systems under consideration, the yields of polymers in copolymerization in the bulk do not exceed 50% even at extremely long reaction time (up to 10 h). In copolymerization in a solution, the yield of copolymer depends on the solvent. In particular, in chloroform the yields of DAPH copolymers are higher than those in the bulk and can reach 70%.

The structure of the copolymers was determined by ^{13}C NMR. In the spectra of copolymers (Table 3) of derivatives of DAHs with SO_2 (nos. 6–8), along with the signals of substituent atoms at the –NHR group, where R is CH_3, C_3H_7, and C_6H_5, there are only three pairs of signals corresponding to two methylene and one methine groups of the polymer chain, which are stereoisomeric. This suggests the structural homogeneity of the copolymers. Two pairs of low-field triplets correspond to *cis*/*trans* stereoisomeric carbon atoms $C^1C^{1'}$ and $C^3C^{3'}$; two doublet signals correspond to stereoisomeric C^2 and $C^{2'}$ atoms of the heterocycle. The relative content of *cis*/*trans* stereoisomeric units of DAH was estimated from the ^{13}C NMR spectrum to be approximately 4/1. The chemical shifts of the above carbon atoms, considering the additive effect of substituents, $-SO_2-$ and NH–R groups, are close to the chemical shifts of the corresponding atoms of the copolymer of *N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride with SO_2 [10]. The chemical shifts of VM units in the spectra of the copolymers are practically the same as those for the corresponding carbon atoms of their homopolymers [12–16]. In the spectra of the copolymers with broad-band proton decoupling, similarly to the spectra of VM homopolymers, there are configuration multiplets belonging to pseudo-asymmetric C^7 atom and adjacent α and β carbon nuclei. These data suggest that the copolymer contains VM blocks alternating with separate DAH units.

The resulting copolymers are soluble in polar solvents such as DMSO and DMF. Copolymers of DAAH with SO_2, AA, and VP are also soluble in water. Preliminary tests showed that copolymers of DAAH with SO_2 have flocculation properties, in particular, in precipitation of $Cu(OH)_2$.

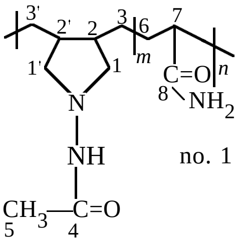
CONCLUSIONS

(1) Derivatives of diallylhydrazines are a new structural type of *N*-allylated monomers promising for production of polyfunctional polymers, among them water-soluble, in radical polymerization.

(2) Diallylhydrazines enter into copolymerization reactions with participation of both double bonds to

Table 3. Chemical shifts and multiplicity of the signals in the ^{13}C NMR spectra of copolymers

Copolymer no.	Stereoisomer	C^1, $C^{1'}$	C^2, $C^{2'}$	C^3, $C^{3'}$	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}
1	*cis*	62.20	40.19	28.09	175.04	21.69	36.19	44.40	182.09			
	trans	62.35	40.88	28.41	174.75	q	37.14	44.18	183.05			
		t	d	t	s		36.82	43.82	s			
							t	d				
2	*cis*	58.96	39.69	25.44	173.71	21.17	32.56	27.86	120.28			
	trans	60.08	41.53	28.73	173.58	19.62	32.88	27.38	120.83			
		t	d	t	s	q	t	26.72	121.94			
								d	s			
3	*cis*	58.76	34.80	29.76	176.74	21.16	43.85	44.38	19.47	177.15	51.60	
	trans	59.32	36.05	32.77	s	q	t	s	18.45	176.17	q	
		t	d	t					q	s		
4	*cis*	59.98	40.25	27.30	178.30	20.40	32.80	66.51	170.15	21.12		
	trans	62.81	43.41	29.94	s	q	31.94	69.31	169.87	19.48		
		t	d	t			t	72.19	s	q		
			34.91	32.77				d				
			35.63	35.44								
			d	t								
5	*cis*	62.25	35.08	29.14	173.54	21.45	31.85	46.25	179.78	33.67	19.95	44.76
	trans	64.85	40.63	32.14	s	q	t	48.06	s	t	t	t
		t	d	t				d				
	cis		38.13									
	trans		41.05									
			d									
6	*cis*	61.90	35.41	54.01	177.13	22.42						
	trans	61.33	37.82	57.02	s	q						
		t	d	t								
7	*cis*	57.80	33.53	52.19	165.51	133.09	127.45	128.55	131.83			
	trans	58.35	36.51	55.45	s	s	d	d	d			
		t	d	t								
8	*cis*	57.41	33.27	52.09	170.73	35.58	18.50	13.45				
	trans	58.04	33.27	55.26	s	t	t	q				
		t	d	t								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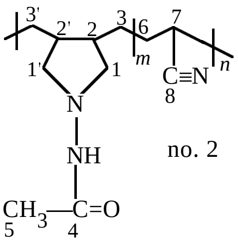
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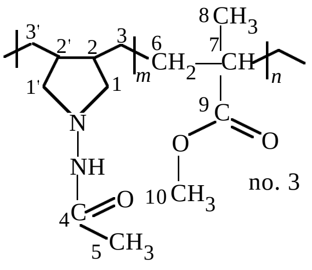
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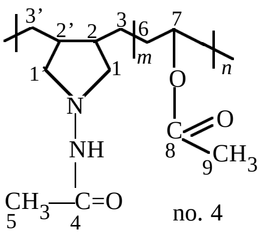
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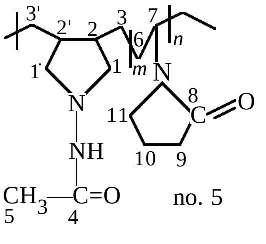
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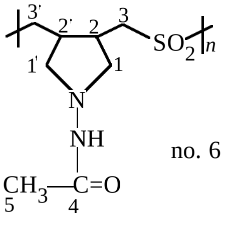
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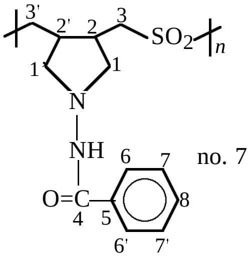
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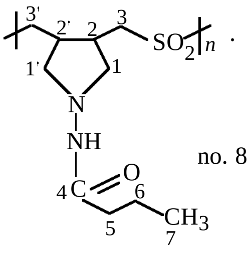
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form soluble cyclolinear polymers of pyrrolidone structures.

(3) Copolymerization of diallylhydrazines with vinyl monomers yields random copolymers, and that with sulfur dioxide, alternating copolymers of equimolar composition.

REFERENCES

1. Topchiev, D.A., Bikasheva, G.T., Martynenko, A.I., *et al.*, *Vysokomol. Soedin.*, *Ser. B*, 1980, vol. 22, no. 4, pp. 269–273.
2. Wandrey, Ch. and Jaeger, W., *Acta Polym.*, 1985, vol. 36, no. 2, pp. 100–102.
3. Vorob'eva, A.I., Kartusheva, E.R., Leplyanin, G.V., *et al.*, *Vysokomol. Soedin.*, *Ser. B*, 2000, vol. 44, no. 5, pp. 868–871.
4. USSR Inventor's Certificate no. 1514759.
5. USSR Inventor's Certificate no. 1744797.
6. RF Patent no. 2095056.
7. Teterina, N.N., Radushev, A.V., Adeev, M.S., and Gusev, V.Yu., *Zh. Prikl. Khim.*, 1995, vol. 68, no. 1, pp. 3–8.
8. Radushev, A.V., Gusev, V.Yu., Bogomazova, V.S., *et al.*, *Zh. Prikl. Khim.*, 1996, vol. 69, no. 8, pp. 1283–1289.
9. Radushev, A.V., Gusev, V.Yu., Bogomazova, V.S., and Kichichin, V.I., *Izv. Vyssh. Uchebn. Zaved.*, *Tsvetn. Metall.*, 1999, no. 6, pp. 28–30.
10. Vorob'eva, A.I., Vasil'eva, E.V., Gaisina, Kh.A., *et al.*, *Vysokomol. Soedin.*, *Ser. A*, 1996, vol. 38, no. 10, pp. 1663–1667.
11. Gur'yanova, E.N., Gol'dshtein, I.P., and Romm, I.P., *Donoro-aktseptornaya svyaz'* (Donor–Acceptor Bond), Moscow: Khimiya, 1973.
12. Bajaj, P., Padmanaban, M., and Gandhi, R.P., *Polymer*, 1985, vol. 26, no. 3, pp. 391–396.
13. Berestova, S.S., Shchirets, V.A., Selikhova, V.I., *et al.*, *Vysokomol. Soedin.*, *Ser. B*, 1996, vol. 38, nos. 9–10, pp. 1612–1613.
14. Lancaster, J.E. and O'Connor, M.N., *J. Polym. Sci.*, *Polym. Lett. Ed.*, 1982, vol. 20, no. 10, pp. 547–550.
15. Moad, G., Solomon, D.H., Spurling, T.H., *et al.*, *Aust. J. Chem.*, 1986, vol. 39, no. 1, pp. 43–50.
16. Cheg, H.N., Smith, T.E., and Virtus, D.M., *J. Polym. Sci.*, *Polym. Lett. Ed.*, 1981, vol. 19, pp. 29–31.