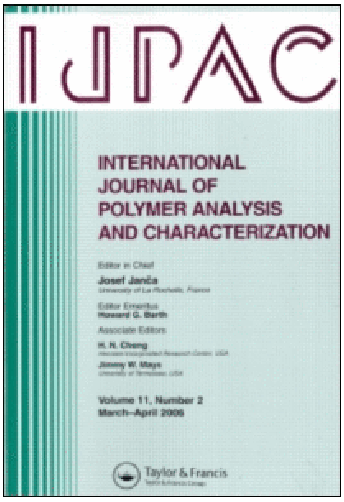


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

NMR for Determining the Structure of New Polysulfones

M. Gorbunova[a]; A. Vorob'eva[b]; R. Muslukhov[b]
[a] Institute of Technical Chemistry, Ural Branch of Russian Academy of Sciences, Perm, Russia [b] Institute of Organic Chemistry, Ufa Scientific Centre of Russian Academy of Sciences, Ufa, Russia

To cite this Article Gorbunova, M. , Vorob'eva, A. and Muslukhov, R.(2009) 'NMR for Determining the Structure of New Polysulfones', International Journal of Polymer Analysis and Characterization, 14: 7, 575 — 587

To link to this Article: DOI: 10.1080/10236660903225445

URL: http://dx.doi.org/10.1080/10236660903225445

International Journal of Polymer Anal. Charact., 14: 575–587, 2009

ISSN 1023-666X print
DOI: 10.1080/10236660903225445

NMR for Determining the Structure of New Polysulfones

M. Gorbunova,[1] A. Vorob'eva,[2] and R. Muslukhov[2]
[1]Institute of Technical Chemistry, Ural Branch of
Russian Academy of Sciences, Perm, Russia
[2]Institute of Organic Chemistry, Ufa Scientific Centre of
Russian Academy of Sciences, Ufa, Russia

Abstract: The reactivity of *N*-allylated monomers of new structural types—*N*, *N*-diallyl-*N′*-acylhydrazines, 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride, and tris(diethylamino)diallylaminophosphonium tetrafluoroborate—and chloride in reactions of free-radical homo- and copolymerization with sulfur dioxide has been studied. The structure of the obtained polysulfones has been identified by ^{13}C NMR. The investigations carried out have shown that these new allyl monomers copolymerize with SO_2, both double bonds participating with formation of cis-, trans-stereoisomeric pyrrolidine structures in a cyclolinear polymer chain. The cyclolinear copolymers obtained are soluble due to the intramolecular cyclization of allyl monomers during the formation of the polymer chain and to the absence of intermolecular cross-links.

Keywords: Allyl monomers; Nuclear magnetic resonance spectroscopy; Radical polymerization; Sulfur dioxide

Submitted 21 May 2009; revised 13 July 2009; accepted 21 July 2009.

Financial support by the Russian Foundation for Basic Research (grant no. 09-03-00220) is gratefully acknowledged.

Correspondence: M. Gorbunova, Institute of Technical Chemistry, Ural Branch of Russian Academy of Sciences, Korolev St., 3, Perm 614013, Russia. E-mail: cheminst@permonline.ru

INTRODUCTION

The primary motivation for determining the structure of a polymer chain is to relate the structure to the performance properties of the polymer in end use. If a polymer chain is completely characterized and the structural basis of its properties is known, the polymerization can be optimized and controlled to produce the best possible properties from the chemical system. Nuclear magnetic resonance (NMR) spectroscopy has proven to be the most effective technique in chemical structure characterization, not only permitting the determination of the copolymer composition but also providing information on detailed structure of the copolymer chains.

Interest in the purposive synthesis of polyfunctional polymers is growing steadily. It is conditioned by a wide set of useful properties of these polymers.[1–5] Among allyl monomers only quaternary salts of diallylammonium have found an application as monomers for the synthesis of polyfunctional polymers.[6–9] It is well known that hydrazides of aliphatic acids possess flotation properties,[10] and they are selective copper extractants.[11] Compounds containing guanidine groups show a broad spectrum of bactericide effects, and they are used as medicines and fungicides.[12,13] Phosphoric polymer derivatives are of significant interest because they are widely used as extractants and complexing agents. Complexation ability of aminopolyphosphonium compounds in reactions with different metals (copper, beryllium, uranium, lead) opens the possibility for their use in the removal of metals from organisms.[14,15]

N-allyl derivatives of hydrazine, diethylaminoguanidine, and aminophosphonium salts are promising as monomers from this point of view. Results of investigations concerning synthesis of new polysulfones and determination of their structure by NMR are presented in this article.

EXPERIMENTAL SECTION

Materials

N, *N*-diallyl-*N*′-acylhydrazines (DAH) were obtained as the result of the interaction of hydrazide of aliphatic or aromatic acids and allyl chloride by the technique described by Gusev et al.[16] and Gorbunova et al.[17]

2,2-Diallyl-1,1,3,3-tetraethylguanidiniumchloride (AGC) was synthesized from tetraethylurea by the technique described by Gorbunova et al.[17] and Vorob'eva et al.[18]

Tris(diethylamino)diallylaminophosphonium tetrafluoroborate (DAAP-BF_4) and chloride (DAAP-Cl) were obtained according to the method described by Vorob'eva et al.[19]

Sulfur dioxide was dried by passing it through concentrated sulfuric acid and just-sintered $CaCl_2$.

Characteristics of applied initiators (potassium persulfate (PP), benzoyl peroxide (BP), 2, 2′-azobisisobutyronitrile (AIBN)) and solvents (dimethyl sulfoxide (DMSO), acetone, chloroform, methanol) conformed to the reference data after purification by conventional methods.

Homo- and Copolymerization

Homo- and copolymerization of DAH, AGC, DAAP-Cl, and DAAP-BF_4 was carried out in bulk and in solution in the presence of initiators AIBN and BP by performing the reaction in bulk and in organic solvent and initiator PP in aqueous medium.

The homopolymerization experiments of allyl monomers were carried out in sealed Pyrex ampoules under vacuum. The contents were frozen, and then the ampoules were degassed under reduced pressure and sealed off. Then the ampoules were introduced into the thermostat at the necessary temperature.

The copolymerization experiments of new allyl monomers with SO_2 were carried out in a glass reactor according to the following technique. A necessary quantity of SO_2 was introduced into a liquid nitrogen-cooled reactor via recondensation stage, then the necessary quantities of allyl monomer, initiator, and solvent were added. After that the reactor was shut and the reaction was carried out at the chosen temperature.

The reaction was allowed to proceed to an extent not passing 10% conversion, at which point the reaction was stopped. Copolymers were precipitated and purified by three-fold reprecipitation by the precipitant from the solution. Solvents and precipitants were selected individually for each system (for DAH-SO_2, DMSO/acetone; for AGC-SO_2, DAAP-Cl-SO_2, and DAAP-BF_4-SO_2, methanol/tetrahydrofurane). The purified copolymers were dried under vacuum at 50°C until constant weight was reached. The copolymer composition was calculated from the elemental analysis data.

Measurements

Molecular weight of copolymers was determined by centrifugation method in methanol at 25°C.

UV spectra were recorded on a Shimadzu UV-VIS-NIS-NIR 3100 spectrometer. The complexation was studied depending on deviations from additivity of absorbance differences of the monomer mixture solutions and the sums of absorbances of each comonomer at the same concentrations. The complex composition was determined by the method of isomolar series.[20]

^{13}C NMR spectra of polysulfones were recorded on a Bruker AM-300 spectrometer operating at 75.47 MHz using broadband proton decoupling and in the JMOD (J-modulated) spin echo mode. D_2O and DMSO-d_6 were used as solvents; 2,2-dimethyl-2-silapentan-5-sulfoacid (DSS) and tetramethylsilane (TMS) were used as internal standards.

RESULTS AND DISCUSSION

Allyl compounds, identified by a tendency to degradative chain transfer to the monomer, are known to exhibit low activity in reactions of radical polymerization.[21]

It was determined that new monomers—*N*, *N*-diallyl-*N′*-acylhydrazines, 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride, and tris(diethylamino) diallylaminophosphonium tetrafluoroborate—and chloride are active in copolymerization with sulfur dioxide exhibiting high electron-acceptor activity.

The molecular weights of DAAH, AGC, DAAP-Cl, and DAAP-BF_4 with SO_2 copolymers are 8000, 10000, 9000, and 18000 g/mol, respectively.

The study of copolymerization of new monomers with SO_2 showed that the content of copolymers obtained did not depend on the monomer ratio, reaction conditions (temperature, nature of initiator, medium), or polymerization degree, and did correspond to DAAH:SO_2 ratio of 1:1.[22]

Composition constancy regardless of the monomer ratio in the reaction mixture suggests that copolymerization of new allyl monomers with SO_2 proceeds via formation of the complexes. A new band of a charge transfer with $\lambda_{max} = 263\,nm$ (Figure 1) was detected in UV spectra of DAAH and SO_2 mixture, recorded in chloroform. Formation of the complex of DAAH with SO_2, becoming apparent as a result of the deviation from additivity of absorbances of DAAH, SO_2, and their mixture, was also detected in DMSO and aqueous solutions (Figure 2). From this figure it is seen that maximum deviation is observed at equimolar ratio of the monomers.

Comparison of DAAH and of its adduct with SO_2 ^{13}C NMR spectra in water shows (Table I) the end C_3 and C'_3 atoms shifting to the weak field area substantially (~9 ppm), as well as the signals of atoms C_2 and C'_2 shifting to the strong field area (~1 ppm). The shifts of the signals of the double bond carbon atoms denote distribution of π-electron density in DAAH molecule and formation of donor-acceptor complex [DAAH $\cdots$ SO_2]. Magnetic equivalence of the carbon atoms of allyl groups indicates that the complex structure is symmetric.

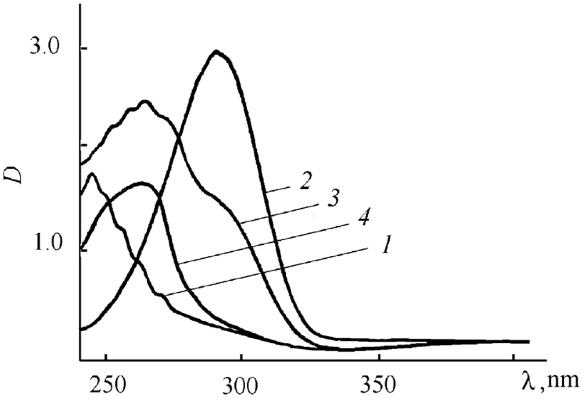


Figure 1. Electron absorption spectra of solutions in chloroform: $[DAAH] = 1.0 \times 10^{-2}\,mol\,L^{-1}$ (1); $[SO_2] = 1.0 \times 10^{-3}\,mol\,L^{-1}$ (2); $[DAAH] = 0.5 \times 10^{-2}$ and $[SO_2] = 0.5 \times 10^{-3}\,mol\,L^{-1}$ mixture (3); spectrum (4) – difference of spectrum (3) and half-sum of spectra (1) and (2).

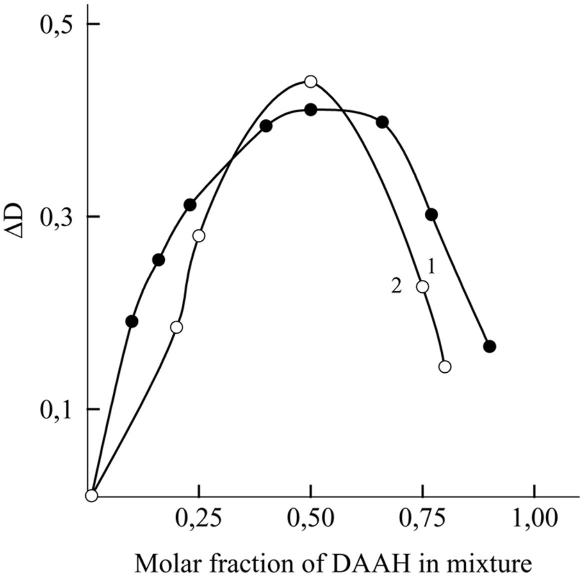
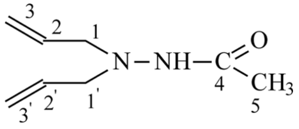
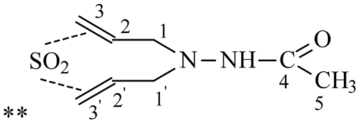
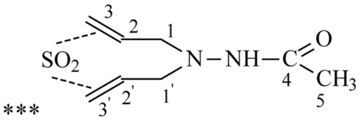


Figure 2. Absorbance difference of solutions of DAAH and SO_2 mixtures and the sum of absorbance of individual solutions of DAAH and SO_2 in water at $\lambda = 277\,nm$ (1) and DMSO at $\lambda = 282\,nm$ (2) vs. their ratio.

Table I. ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of DAAH and its complex with SO_2

No.	Formula	Chemical shift values (δ, ppm) and signal multiplets of the atoms				
		C_1, C_1'	C_2, C_2'	C_3, C_3'	C_4	C_5
1		59.11 t	132.12 d	117.14 t	172.15 s	18.69 q
2		62.79 t	131.16 d	126.51 t	174.24 s	22.24 q
3		60.49 t	134.58 d	118.72 t	173.22 s	20.40 q

, in H_2O; *, in DMSO.

Elemental analysis showed that the copolymer of equimolar composition was formed irrespective of the monomer ratio. A question arose: will the copolymer be formed with participation of one or two allyl groups? There are no signals of carbon atoms C_6, C_7, C_8 (Figure 3) in NMR ^{13}C polysulfone spectra (chemical shifts of C_6, C_7, C_8 carbon atoms were determined using spectral data for DAAH), and therefore copolymerization proceeds with participation of both double bonds.

The copolymers obtained are soluble, therefore the intermolecular cross-links are absent, which is why copolymerization proceeds via intramolecular cyclization of *N*, *N*-diallyl-*N*′-acetylhydrazine and formation of piperidine ring (Figure 3, structure I) or pyrrolidine ring (Figure 3, structure III). Structure II (Figure 3), obtained by intermolecular cyclization with formation of 1,4-thiazan-1,1-dioxide ring, is also possible.

Table II presents the calculated values of chemical shifts for structures I, II, and III and experimental spectrum. Chemical shifts of carbon atoms were determined using literature spectral data[23] for substituted pyrrolidines. The additive influence of SO_2-group on chemical shifts of carbon atoms of copolymers was taken into account. Ten signals are observed in the copolymer spectrum. However, for structure I the absence of symmetry is characteristic, and it should result

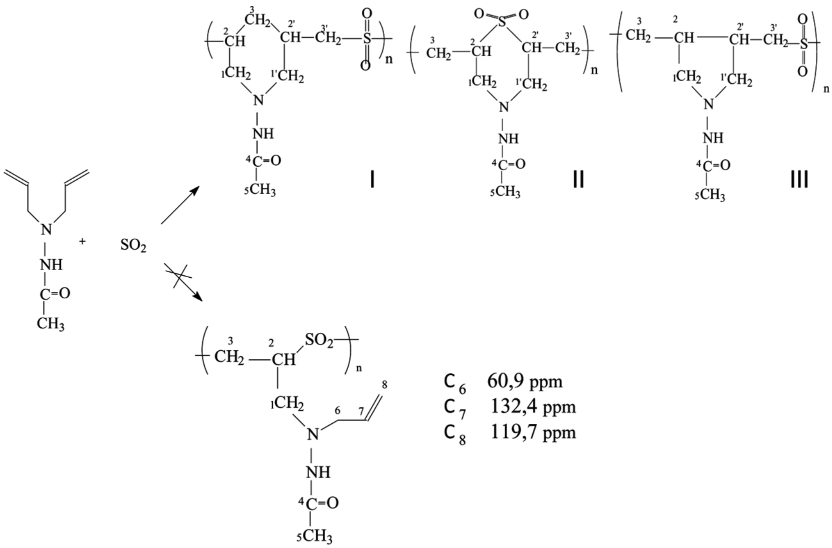


Figure 3. Copolymerization of DAAH with SO_2.

in the appearance of nonequivalent signals. Structure II is also not confirmed because doublet signals of C_2 and C'_2 atoms connected with SO_2-groups should be observed in the weaker field area (60–70 ppm) as compared with triplet signals of C_3 and C'_3 atoms (30–40 ppm).

Table II. Experimental ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of DAAH copolymers with SO_2 and the calculated chemical shift values and signal multiplets of the atoms for structures I–III (Figure 3) (D_2O, DSS, 25°C)

	Chemical shift values and signal multiplets of the atoms				
Structure	C_1, C'_1	C_2, C'_2	C_3, C'_3	C_4	C_5
I	60–70	60–70; 30–40	30–40; 50–60	170–180	20–30
	t	d d	t t	s	q
II	60–70	60–70	30–40	170–180	20–30
	t	d	t	s	q
III	60–70	30–40	50–60	170–180	20–30
	t	d	t	s	q
Experimental spectrum					
Cis	61.30	35,18	54,13	173.60	22.54
	t	d	t	s	q
Trans	62.64	37,64	57,19	174.16	21.89
	t	d	t	s	q

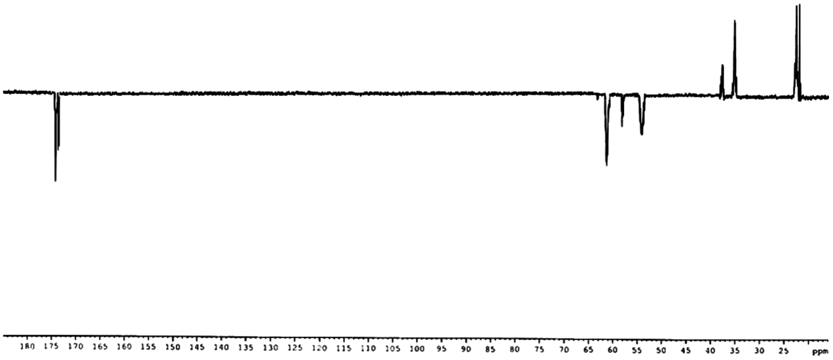


Figure 4. ^{13}C NMR spectrum of DAAH polysulfone (JMOD, D_2O, DSS, +25°C).

In the spectra of DAAH polysulfone (Figure 4) there are only two couples of the weak-field triplet signals of stereoisomeric C_3, C'_3 (54.13, 57.19 ppm) and C_1, C'_1 (61.30, 62.64 ppm) atoms connected with SO_2- and CH_3CONHN– groups, respectively, a couple of doublet signals at 35.18, 37.64 ppm, which are attributable to tertiary C_2, C'_2 atoms of stereoisomeric copolymer, and signals of acetyl group.

In two-dimensional COSY spectra cross-peaks indicating the difference in chemical shifts of pseudoaxial and pseudoequatorial heminal NCH_2 protons can be seen, which are characteristic for five-member heterocycles. That is why on the basis of these data we can conclude that cis-, trans-isomeric cycle copolymer with di-substituted pyrrolidinium units was obtained.

Blocks of DAAH homopolymer are absent in the polysulfone structure as the ^{13}C NMR spectrum does not contain strong-field triplet signals of two cis-, trans-methylene groups C_3, C'_3 at 27.31 ppm (Figure 5), which are analogous to that for homopolymer.

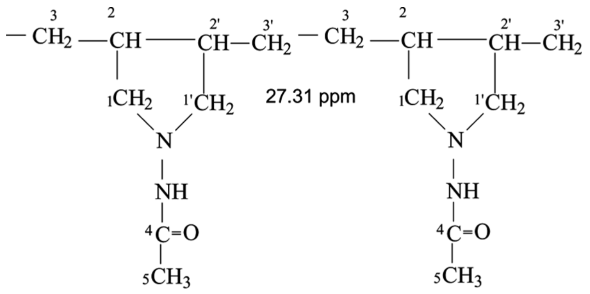
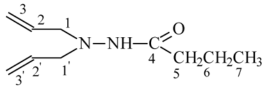
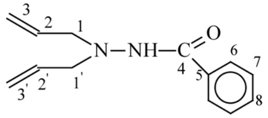
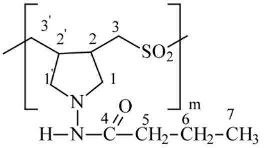
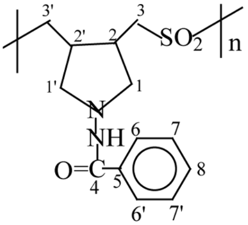


Figure 5. Blocks of DAAH homopolymer.

Table III. ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of DAH and their copolymers (DMSO, TMS, 25°C)

No.	Formula	Chemical shift values (δ, ppm) and signal multiplets of the atoms								
		*	C_1, C_1'	C_2, C_2'	C_3, C_3'	C_4	C_5	C_6	C_7	C_8
1			57.2	132.5	115.2	169.0	32.3	16.4	11.75	
			t	d	t	s	t	t	q	
2			58.83	134.9	117.4	165.3	134.1	127.1	128.1	131.0
			t	d	t	s	s	d	d	d
3		c	57.41	33.27	52.09	170.7	35.58	18.50	13.45	
		t	58.04	33.28	55.26	s	t	t	q	
			t	d	t					
4		c	57.80	33.53	52.19	165.5	133.1	127.5	128.6	131.8
		t	58.35	36.51	55.45	s	s	d	d	d
			t	d	t					

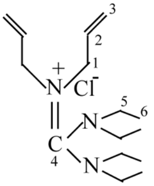
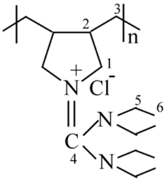
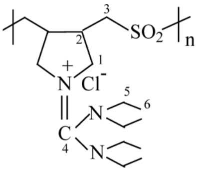
*Stereoisomers: c = cis, t = trans.

Analysis of presented copolymer spectra shows DAAH to copolymerize with SO_2 with formation of cis-, trans-stereoisomeric pyrrolidine structures in a cyclolinear polymer chain in the proportion ~4:1.

The spectra of copolymers of the other DAH with SO_2 are similar (Table III). In the spectra of copolymers of other DAH with SO_2 there are two couples of the weak-field triplet signals of stereoisomeric C_3, C_3' and C_1, C_1', a couple of doublet signals of C_2, C_2' atoms, values of chemical shifts close to those given for copolymers of DAAH with SO_2, and signals of buthanoyl and benzoyl groups.

In the spectra of homopolymer of AGC and copolymer with SO_2 (Table IV), except for the signals of carbon atoms (C_5, C_6) of two magnetic-equivalent groups $-N(-\underline{C}H_2-\underline{C}H_3)_2$ and singlet signal of C_4 atom of group $=\underline{C}\{-N(-CH_2-CH_3)_2\}_2$, there are only two couples of triplet (C_1, C_1' and C_3, C_3') and a couple of doublet (C_2, C_2') signals.

Table IV. ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of AGC and its copolymers (D_2O, DSS, 25°C)

		Chemical shift values (δ, ppm) and signal multiplets of the atoms					
No.	Formula	C_1	C_2	C_3	C_4	C_5	C_6
1		54.56 t	133.70 d	123.40 t	165.70 s	45.83 t	14.48 q
2		55.60 t	43.49 d	27.77 t	162.30 s	45.08 t	14.95 q
3		55.05 t	36.76 d	50.96 t	162.00 s	46.23 t	14.30 q

In the spectra of AGC polysulfone, the values of chemical shifts for cis-, trans-stereoisomers do not differ. A couple of triplet signals of C_1, C_1' atoms and a couple of doublet signals of C_2, C_2' atoms in stereoisomeric pyrrolidinium cycle have similar values of chemical shifts; it is given by the flatted structure of five-member heterocycle with Sp^2-hybridized N atom, which has a flat trigonal configuration of bonds. Analysis of presented AGC polysulfone spectra shows AGC to copolymerize with SO_2 with formation of cis-, trans-stereoisomeric pyrrolidine structures in cyclolinear polymer chain in the proportion ~5:1.

Analysis of ^{13}C NMR spectra of DAAP-BF_4 and DAAP-CI with SO_2 mixtures shows the availability of a visible shift of signals of allyl group carbon atoms (as compared with monomers), which indicates the formation of donor-acceptor complex of the monomers with SO_2 (Table V). However, the values of these shifts are much greater than with diallylacylhydrazines. Perhaps, in the case of diallylaminophosphonium salts, P and N atoms of electrodonor groups P-(N-C_2H_5)$_2$ take part in complexation. In ^{13}C NMR spectra of polysulfones (Table VI) there are

Table V. ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of DAAP-Cl (1), DAAP-BF$_4$ (3), and their complexes (2, 4) with SO$_2$ (DMSO-d$_6$, TMS, 25°C)

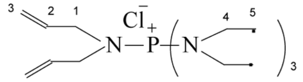
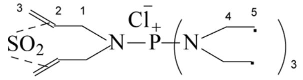
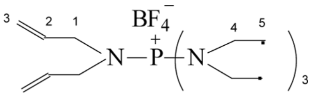
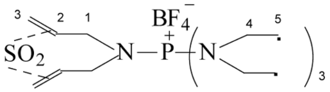
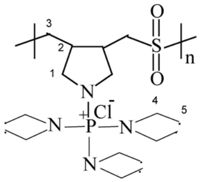
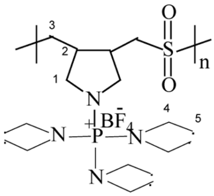
No.	Formula	Chemical shift values (δ, ppm) and signal multiplets of the atoms				
		C$_1$	C$_2$	C$_3$	C$_4$	C$_5$
1		49.65 t	134.08 d	119.65 t	41.02 t	13.73 q
2		43.01 t	136.00 d	115.48 t	39.44 t	12.75 q
3		49.27 t	132.54 d	119.58 t	40.58 t	13.09 q
4		43.10 t	135.67 d	115.66 t	40.25 t	13.25 q

Table VI. ^{13}C NMR spectral parameters (chemical shifts and multiplicities) of DAAP-Cl, DAAP-BF$_4$ copolymers with SO$_2$ (DMSO-d$_6$, TMS, 25°C)

No.	Formula	*	Chemical shift values (δ, ppm) and signals multiplets of the atoms				
			C$_1$, C$'_1$	C$_2$, C$'_2$	C$_3$, C$'_3$	C$_4$	C$_5$
1		c t	52.60 53.34 t	36.71 38.77 d	51.98 54.82 t	41.27 40.37 t	13.94 13.94 q
2		c t	50.57 51.04 t	34.90 36.94 d	50.42 52.14 t	39.40 39.35 t	12.93 12.43 q

*Stereoisomers: c = cis, t = trans.

two couples of weak-field triplet signals of cis/trans-isomeric C_1, C_1' and C_3, C_3' atoms, and also a couple of doublet signals of C_2, C_2' atoms. The content of cis-stereoisomeric units in polysulfones (DAAP-BF_4 with SO_2 and DAAP-Cl with SO_2) is higher than that of trans-units (7:1 and 5:1, respectively).

CONCLUSIONS

Our results indicate that the proposed approach based on ^{13}C NMR spectroscopy is suitable for the characterization of new polysulfones. It has been determined that *N*, *N*-diallyl-*N*′-acylhydrazines, 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride, tris(diethylamino) diallylam inophosphonium tetrafluoroborate, and chloride exhibit high activity in copolymerization with sulfur dioxide. Copolymerization proceeds via complexation, resulting in alternating copolymers of equimolar composition independently of the monomer ratio in the initial mixture and of the reaction conditions. New *N*-allyl monomers copolymerize with SO_2 with formation of cis-, trans-stereoisomeric pyrrolidine structures in cyclolinear polymer chain.

REFERENCES

[1] Kirsh, Yu. E. (1988). *Poly-N-Vinylpyrrolidone and Other Poly-N-Vinylamides: Synthesis and Physico-Chemical Properties*. Moscow: Nauka, p. 252.

[2] Al-Issa, M. A., T. P. Davis, M. B. Huglin, and D. C. F. Yip. (1985). Copolymerization involving *N*-vinyl-2-pyrrolidone. *Polymer* **26**, 1869–1874.

[3] Soundararajan, S., and B. S. R. Reddy. (1993). Synthesis, characterization and the reactivity ratios of copolymers of cyclohexyl acrylate with styrene and *N*-vinyl-2-pyrrolidone. *Polymer* **34**, 2224–2226.

[4] Wen, Sh., Y. Xiaonan, and W. T. K. Stevenson. (1992). Free radical solution copolymerization of glycidyl methacrylate with *N*-vinyl pyrrolidone. *Polym. Int.* **27**, 81–85.

[5] Boyarkina, N. M., V. V. Kryuchkov, E. S. Parkhamovich, L. A. Amburg, D. A. Topchiev, and V. A. Kabanov. (1987). Polymers on the base of N,N-dimethyl-N,N-diallylammonium chloride. *Plast. Mass.* **8**, 17–20.

[6] Butler, G. B., and R. J. Angelo. (1957). Preparation and polymerization of unsaturated quaternary ammonium compounds. VIII. A proposed alternating intramolecular-intermolecular chain propagation. *J. Am. Chem. Soc.* **79**(12), 3128–3131.

[7] Wandrey, Ch., and W. Jaeger. (1985). Copolymerization of dimethyldiallylammonium chloride and acrylamide. *Acta. Polym.* **36**, 100–102.

[8] Harada, S., and K. Arai. (1967). The cyclo-copolymerization of diallyl compounds and sulfur dioxide. *Makromol. Chem.* **107**, 64–77.

[9] Vorob'eva, A. I., Y. A. Prochuhan, and Y. B. Monakov. (2003). Allyl compounds in radical polymerization reactions. *Polym. Sci.* **45**, 2118–2136.

[10] Teterina, N. N., A. V. Radushev, M. S. Adeev, and V. Y. Gusev. (1995). Hydrazides of carbon acids as collectors at flotation of potassium chloride from potassic ores. *Russ. J. Appl. Chem.* **68**, 3–8.

[11] Radushev, A. V., V. Y. Gusev, G. S. Bogomazova, A. M. Kopanev, and G. K. Kulmukhamedov. (1996). Hydrazides of carbon acids as Cu (II) extactants. *Russ. J. Appl. Chem.* **69**, 1283–1289.

[12] Malkanduev, Yu. A., S. Y. Khashirova, and N. A. Sivov. (2003). Radical copolymerization of *N*, *N*-diallylquanidinacetate and *N*, *N*-dimethyl-*N*, *N*-diallylammonium chloride. *Vestnik Kabardino-Balkar. Univ.* **5**, 62–66.

[13] Topchiev, D. A., and Y. A. Malkanduev. (2004). *Cationic Polyelectrolytes: Obtaining, Properties and Using*. Moscow: Akademkniga, p. 232.

[14] Kabachnik, M. I., T. Y. Medved, N. M. Dyatlova, O. G. Arkhipova, and M. V. Rudomino. (1968). Organophosphorous complexones. *Usp. Him.* **37**, 1161–1191.

[15] Arkhipova, O. G., T. A. Kochetkova, M. V. Rudomino, T. Y. Medved, and M. I. Kabachnik. (1964). Influence of aminoalkylphosphinic acids on the experimental beryllium poisoning. *Dokl. Akad. Nauk SSSR*. **158**, 1235–1237.

[16] Gusev, V. Yu., A. I. Vorob'eva, A. V. Radushev, S. V. Kolesov, R. R. Muslukhov, and A. G. Tolstikov. (2003). Diallylacylhydrazines as monomers for polyfunctional water-soluble polymers. *Dokl. RAN* **12**, 2603–2605.

[17] Gorbunova, M. N., A. I. Vorob'eva, A. G. Tolstikov, and Y. B. Monakov. (2009). New N-allylated monomers in the synthesis of practical valuable high-molecular-weight compounds. *Polym. Adv. Technol.* **20**, 209–215.

[18] Vorob'eva, A. I., D. R. Sagitova, M. N. Gorbunova, R. R. Muslukhov, S. V. Kolesov, A. G. Tolstikov, and Y. B. Monakov. (2007). Activity of diallylamido-bis-(diethylamido)quanidinium chloride in radical polymerization reactions. *Polym. Sci.* **49**, 1293–1298.

[19] Vorob'eva, A. I., M. N. Gorbunova, F. A. Sataeva, R. R. Muslukhov, S. V. Kolesov, A. G. Tolstikov, and Y. B. Monakov. (2008). Diallylamidophosphonium salts in radical polymerization reaction. *Russ. J. Appl. Chem.* **81**, 803–807.

[20] Guryanov, E. N., I. P. Goldstein, and I. P. Romm. (1973). *Donor-Acceptor Bond*. Moscow: Khimiya, p. 397.

[21] Kabanov, V. A., V. P. Zubov, and Y. D. Semchikov. (1987). *Complex-Radical Polymerization*. Moscow: Khimiya, p. 256.

[22] Vorob'eva, A. I., M. N. Gorbunova, S. I. Kuznetsov, R. R. Muslukhov, S. V. Kolesov, A. G. Tolstikov, and Y. B. Monakov. (2006). In *Order and Disorder in Polymer Reactivity*, eds. G. E. Zaikov and B. A. Howell. New York: Nova Science Publishers, pp. 125–136.

[23] Clerk, P., and S. Simon. (1983). *Spectral Data for Structure Determination of Organic Compounds*. Berlin: Springer-Verlag, p. 380.