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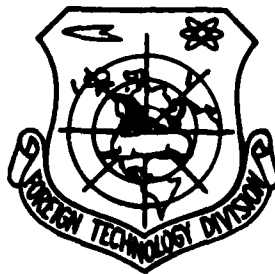
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HIGH-MOLECULAR COMPOUNDS  
(Selected Articles)



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# HUMAN TRANSLATION

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TABLE OF CONTENTS

U.S. Board on Geographic Names Transliteration System .....	ii
Two-Stage Synthesis of Poly-2,6-Benzothiazoles, by V.V. Korshak, M.M. Teplyakov, A.D. Maksimov .....	1
The Nature of the Orientation of Folded Structures in Elastomers Under Tension, by A.S. Shashkov, F.A. Galil-Ogly, A.S. Novikov .....	6

## U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З э	<i>З э</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\*ye initially, after vowels, and after ъ, ь; e elsewhere.  
When written as ѣ in Russian, transliterate as yě or ě.

### RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh <sup>-1</sup>
cos	cos	ch	cosh	arc ch	cosh <sup>-1</sup>
tg	tan	th	tanh	arc th	tanh <sup>-1</sup>
ctg	cot	cth	coth	arc cth	coth <sup>-1</sup>
sec	sec	sch	sech	arc sch	sech <sup>-1</sup>
cosec	csc	csch	csch	arc csch	csch <sup>-1</sup>

Russian	English
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rot	curl
lg	log

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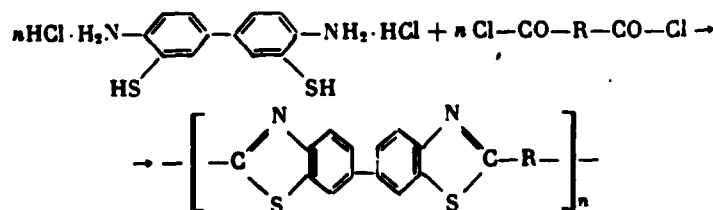
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## TWO-STAGE SYNTHESIS OF POLY-2,6-BENZOTHAZOLES\*

V. V. Korshak, M. M. Teplyakov and A. D. Maksimov  
 Institute of Chemical Engineering imeni D. I. Mendeleev,  
 Moscow

Studies have recently appeared in the literature concerning the synthesis of poly-2,6-benzothiazoles (PBT) at high temperatures in a solvent [1-3]. Aromatic PBT exhibit exceptionally good resistance to heat and chemicals but cannot be dissolved in any of the organic solvents.

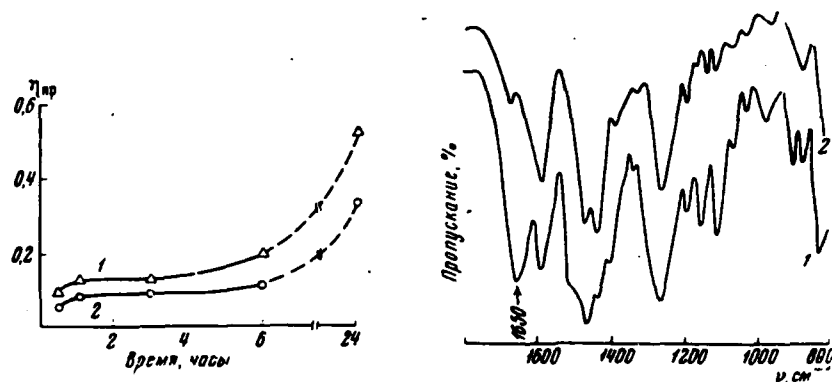
The object of the present study was to synthesize PBT in two stages, attempting in the first stage to obtain noncyclized polymers which would be soluble in organic solvents and to produce a number of new polymers. The formation of PBT may be represented by the following scheme:



First-stage procedure involved low-temperature polycondensation in dimethyl acetamide (DMA) [4]. Figure 1 shows the reduced viscosity of a polymer produced from 3,3'-dimercap-

\* Material presented at a science and technology conference sponsored by the D. I. Mendeleev Institute of Chemical Engineering in Moscow in November 1965.

tobenzidine dihydrochloride and isophthaloyl chloride as a function of reaction time. Figure 1 shows that at  $-20^{\circ}$ , the increase in reduced viscosity ceases after two hours; further increase occurs only after the reaction mixture stands for an extended period at room temperature. The addition of pyridine as a hydrogen chloride acceptor did not increase the viscosity of the polymer.



**Figure 1.** Reduced viscosity of first-stage polymer containing DMA and isophthaloyl chloride as a function of reaction time:

1 - in the absence of pyridine; 2 - in the presence of pyridine (4 moles per 1 mole DMB); abscissa - time in hours



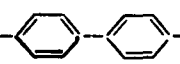
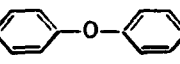
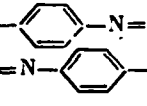





**Figure 2.** IR spectra of noncyclized (1) and cyclized (2) polymers containing DMB and isophthaloyl chloride; y-axis - transmission, %

Polymers containing DMB and adipic, sebacic and isophthalic acids were dissolved in cresol, dimethylformamide and dimethyl sulfoxide under heat. Mixed polymers containing isophthalic and sebacic and isophthalic and terephthalic acids (in molar ratios of 1:1) did not improve solubility.

The second stage in the synthesis of PBT consisted in the polycyclization of polymers obtained in the first stage in a vacuum at  $300^{\circ}$ . The formation of polycyclic polymers was confirmed by elementary analysis, findings of which are presented in the table, as well as by IR spectroscopy (Fig. 2). Figure 2 shows that the transition from the noncyclized polymer to PBT is accompanied by the disappearance of the band of heavy absorption in the vicinity of  $1650\text{ cm}^{-1}$ , which is characteristic of the stretching vibrations of the carbonyl group.

The homo- and mixed PBT were powders which were not soluble in organic solvents but did dissolve without decomposition in concentrated  $\text{H}_2\text{SO}_4$ .

Properties of products of the reaction of DMB with the acid chlorides of dicarboxylic acids

Полимер. № (3)	-R-	I стадия (1)		T. раз- мльч., °C (7)	η <sub>пр.</sub> дл/г	II стадия (2)		
		η <sub>пр.</sub> дл/г	элементарный сос- тав. % (4)			элементарный сос- тав. % (4)		
			вычислено (5)				найде- но (6)	вычислено (5)
1	-(CH <sub>2</sub> ) <sub>6</sub> -	0,18	C 60,30 H 5,06 N 7,81 S 17,88	60,91 5,30 7,61 16,32	325	0,19	C 67,04 H 4,37 N 8,68 S 19,88	68,80 4,48 8,11 19,01
2	-(CH <sub>2</sub> ) <sub>6</sub> -	0,10	C 63,73 H 6,30 N 6,75 S 15,47	64,32 6,83 6,74 14,98	100	0,12	C 69,80 H 5,85 N 7,40 S 16,94	69,97 5,95 7,15 16,38
3		0,54	C 63,46 H 3,70 N 7,13 S 16,91	64,08 3,65 7,40 16,94	320	0,52	C 70,15 H 2,94 N 8,18 S 18,72	70,80 2,82 8,13 18,14
4		0,74	C 63,46 H 3,70 N 7,13 S 16,91	63,88 3,84 7,26 15,30	600	0,73	C 70,15 H 2,94 N 8,18 S 18,72	70,92 2,42 7,92 17,99
5		0,24	C 68,69 H 3,99 N 6,16 S 14,10	69,95 4,20 6,07 13,62	400	0,25	C 74,61 H 3,37 N 6,70 S 15,32	74,82 3,61 6,57 14,55
6		0,18	C 66,36 H 3,85 N 5,95 S 13,62	67,65 3,20 5,68 14,09	400	0,19	C 71,86 H 3,24 N 6,45 S 14,76	72,35 3,57 6,22 14,70
7		0,25	C 67,71 H 3,75 N 11,60 S 13,27	65,23 3,40 9,65 13,64	350	0,25	C 69,93 H 3,16 N 12,54 S 14,36	70,03 3,38 12,12 14,31
8		0,32	C 58,68 H 3,28 N 7,63 S 17,40	60,11 3,65 7,34 16,48	450	0,36	C 65,04 H 2,42 N 8,43 S 19,29	66,76 2,61 8,13 18,78
9	-(CH <sub>2</sub> ) <sub>6</sub> - 	0,14	C 63,59 H 5,08 N 6,95 S 16,20	64,30 5,20 6,23 15,50	220	0,15	C 69,97 H 4,39 N 7,79 S 17,83	70,61 4,25 7,42 17,41
10	  	0,42	C 63,46 H 3,70 N 7,13 S 16,91	63,80 3,59 7,42 16,79	350	0,42	C 70,15 H 2,94 N 8,18 S 18,72	70,12 3,00 8,01 18,52

KEY: 1 - stage 1; 2 - stage 2; 3 - polymer; 4 - elementary composition; 5 - computed; 6 - found; 7 - softening temperature

Thermogravimetric analysis was employed to study the thermal stability of PBT (Fig. 3). The PBT containing the aliphatic acids was found to be considerably lower than that of PBT containing the aromatic acids. Exhibiting the highest thermal stability are the PBT containing the isophthalic, terephthalic and 4,4'-diphenyldicarboxylic acids and 4,4'-dicarboxydiphenyl oxide.

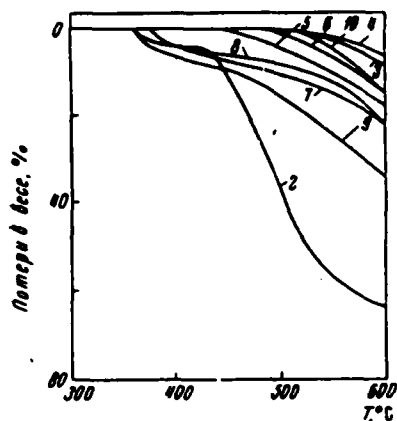


Figure 3. Thermogravimetric curves of PBT (in air; rate of temperature increase 10°/min). Curve numbers correspond to the polymer numbers used in the table; y-axis - weight loss, %

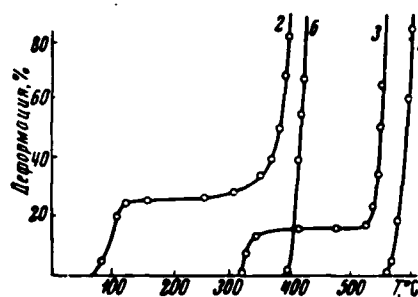


Figure 4. Thermomechanical curves for PBT. Curve numbers correspond to polymer numbers used in the table; y-axis - deformation, %

Figure 4 shows thermomechanical curves for a number of PBT, where we can see that the addition of methylene groups to the main chain of the PBT macromolecule degrades not only the thermal stability, but the deformation temperature of these materials as well.

#### Experimental procedure

*DMB dihydrochloride* was obtained by the Herz reaction; decomposition temperature - 216°. Results, %: S 20.07%.  $C_{12}H_{14}N_2Cl_2S_2$ . Computed, %: S 19.99.

*Acid chlorides of the dicarboxylic acids* were obtained by processing the acids with thionyl chloride. The melting temperatures of the acid chlorides of the aromatic acids and the boiling points of the aliphatic acids agreed with data in the literature [6-11].

*Synthesizing the PBT.* Solid chloride of the carboxylic acid was continuously added to a solution of DMB in DMA at -20° in a flow of nitrogen, the material being agitated vigorously during the process. The polymer was then precipitated by water and rinsed until it no longer reacted to the chlorine ion. The polymers were polycyclized in a vacuum (1 mm) at 300° for 5 h. The reduced viscosity of 0.5% solutions of the polymers in concentrated  $H_2SO_4$  was determined at 20°.

## Conclusions

1. A two-stage procedure is used to produce poly-2,6-benzothiazoles; the first-stage procedure yields polymers which are soluble in organic solvents.

2. New homo- and mixed poly-2,6-benzothiazoles have been obtained which exhibit high degrees of resistance to heat.

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## THE NATURE OF THE ORIENTATION OF FOLDED STRUCTURES IN ELASTOMERS UNDER TENSION

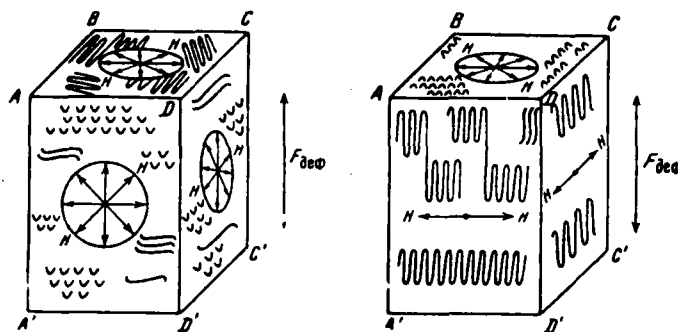
*A. S. Shashkov, F. A. Galil-Ogly and A. S. Novikov*

Ever since Kargin et al. conducted their electron microscope studies it has been generally assumed that the most characteristic supramolecular formations in rubber are the folded structures. An NMR [nuclear magnetic resonance] technique can yield more information of great interest concerning the microstructure of the folded formations and the nature of the configuration of the macromolecules within them.

Most importantly, comparison of NMR data obtained for a number stretched and frozen elastomers [4, 5] with findings from electron microscope investigations [3] shows that folded structures visible through the microscope cannot be primary folds or stacks of macromolecules. The work of Kargin et al. [3] has in fact shown that folded structures in replicas taken from rubber which has been stretched and then frozen will be visible only in the plane perpendicular to the axis along which the material is stretched. If these had been primary folds or stacks of macromolecules (which would be highly unlikely, given the dimensions of the folded structures visible through the microscope), we should not have observed an angular dependence of the second moment  $\Delta H_2^2$  of the NMR absorption line in the case of a number of elastomers, stretched samples of which had been rotated around an axis perpendicular to plane  $AA'DD'$  (or  $DD'CC'$ ) (Fig. 1, a). Among these elastomers would be, for example, the chloroprene and butadiene acrylonitrile rubbers. Making the major contribution to the second moment of the NMR absorption line in these polymers are methylene groups arranged in a circular pattern in the plane perpendicular to the axis of the macromolecule. If, now, the macromolecules themselves are arranged as shown in Fig. 1, a, we would observe full isotropy in the H-H configuration of the methylene groups in the planes

$AA'DD'$  or  $DD'CC'$ , which assumes that there is no angular dependence of the second moment on the angle between the axis of tension and the direction of the constant magnetic field. This dependence has also been observed in the case of stretched samples of chloroprene, butadiene acrylonitrile and other rubbers [4, 5].

It follows from concrete analysis of this angular dependence that the planes of the folds of the macromolecules must lie parallel to the axis of tension as shown in Fig. 1, b. Figure 2 illustrates the theoretical angular dependence in this instance of the second moment of two elastomers placed under tension and then frozen as computed in the first approximation approximation (which takes no account, for example, of the disorienting effect of the methylene groups in the vicinity of the stacks or folds in the macromolecules). Figure 2



**Figure 1.** Possible arrangement of folded macromolecules or stacks in elastomer film under tension. Arrows indicate arrangement of interproton vectors of the methylene groups, assuming ideally oriented supramolecular structures.

shows experimental angular dependences  $\Delta H_2^2$  for the chloroprene and nitrile rubbers. As can be observed from a comparison of the the curves, the model in Fig. 1, b illustrates the experimental angular dependence clearly. The difference between the amplitudes of the computed and experimental curves indicates only that the computations did not take account of all factors disturbing the ideal orientation of the interproton vectors. As far as the particular nature of these dependences is concerned (the location of the minimums and the relative "height" of the right and left branches), this will be governed entirely by the orientation of the interproton vectors, and the orientation of the interproton vectors of the methylene groups perpendicular to the axis of the molecule in particular.

Therefore, taking account of the fact that data from NMR studies of elastomers will in fact correspond only to the model illustrated in Fig. 1, b, we can conclude that the folded structures visible in thin cross sections of stretched and frozen elastomers derive from a secondary origin. They are in fact improperly curved "planes," such as the  $dI$  structure shown in Fig. 3, of what are, strictly speaking, bands. If we assume that the height of the primary zigzag  $h$  of the macromolecules or stacks is much shorter than the "width"  $d$ , and

particularly of the "length"  $l$ , of these structures (which is entirely in line with current thinking on band structures), we can begin to see why the longitudinal section of the stretched elastomers is more uniform than the cross section.

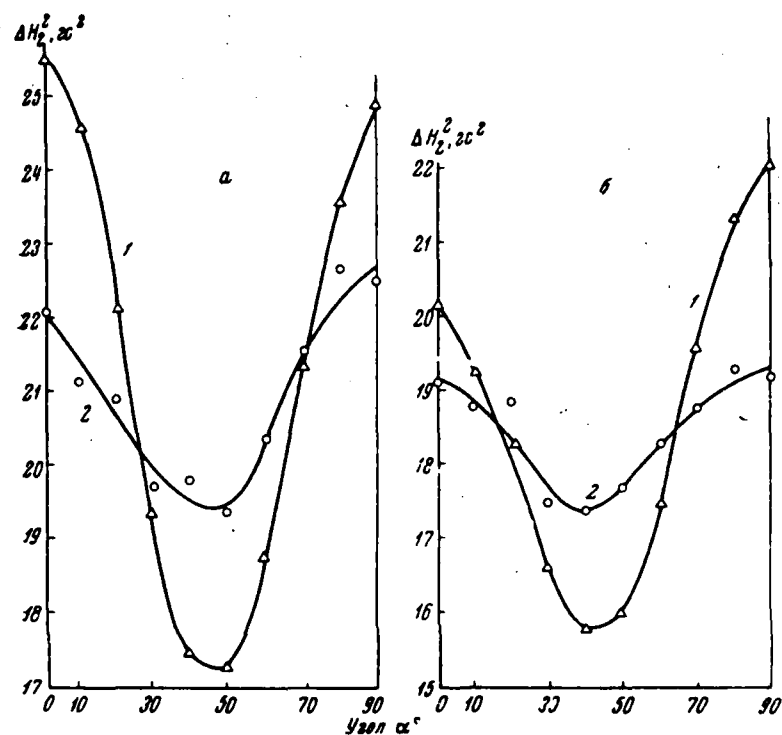


Figure 2. Second moment  $\Delta H_z^2$  of butadiene acrylonitrile (a) and chloroprene (b) rubber as a function of angle  $\alpha$  between axis of tension and the direction of the constant magnetic field:  
1 - computed; 2 - experimental curves

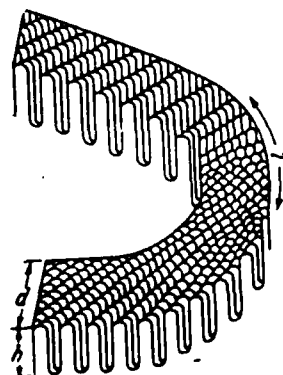


Figure 3. Band structure

Reviewing, now, our discussion here, we can conclude that NMR data for elastomers under tension confirm current thinking concerning the structure of folded structures and the suggestion that the bands involved here lie in a plane perpendicular to the axis of the tension to which the material is subjected [3].

### Conclusions

NMR data on the angular dependence of the second moment of rubber under tension confirm current thinking on the configuration of folded structures and the orientation of the bands in planes perpendicular to the axis of tension to which the elastomer is subjected.

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