Synthesis and investigation of polyphenyldimethylsiloxane block copolymers with bimodal chain length distribution of oligodimethylsiloxane blocks

A. Yu. Rabkina, B. G. Zavin, L. I. Kuteinikova, I. I. Dubovik, M. N. Il'ina, M. V. Gerasimov, and V. S. Papkov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: rabkina@ineos.ac.ru

Siloxane block copolymers containing linear dimethylsiloxane (DMS) and cyclolinear phenylsilsesquioxane blocks were synthesized. A peculiarity of the copolymers is a bimodal distribution of linear DMS blocks in the polymer chain. The results of X-ray diffraction, thermomechanical, and DSC studies of bimodal block copolymers indicate a higher degree of microphase separation of the blocks as compared to unimodal block copolymers.

Key words: siloxanes, block copolymers, bimodal distribution, differential scanning calorimetry, X-ray phase analysis, thermomechanical analysis.

Block copolymers containing flexible blocks with low glass transition or melting temperatures (T_g and T_m, respectively) can behave as elastomers over a wide temperature range. The macromolecules of such elastomers are, as a rule, linked by physical junctions (*e.g.*, crystalline or amorphous glassy domains consisting of blocks of the second component of the copolymer with higher T_g and T_m, which are formed as a result of microphase separation). These junctions are rather strong, hence block copolymers can be used in designing polymeric materials with improved strength properties.[1] In this connection, it was of interest to synthesize siloxane block copolymers containing both flexible polyorganosiloxane blocks and blocks capable of forming strong physical junctions, since nonfilled siloxane rubbers possess low strength properties due to the low cohesive energy of polyorganosiloxanes.

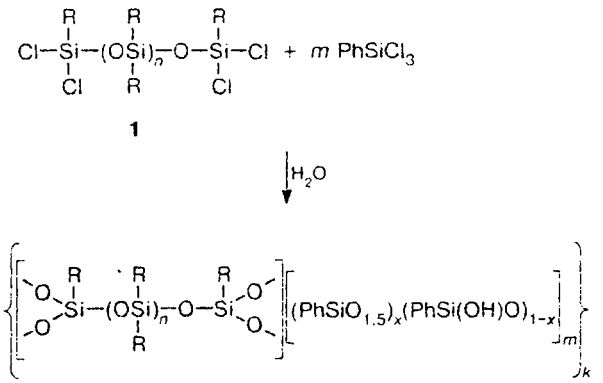
Among the most interesting representatives of this type of block copolymers (BC) are polyphenyldimethylsiloxanes with the general formula $[Me_2SiO]_n[PhSiO_{1.5}]_m$, consisting of alternating flexible dimethylsiloxane (DMS) and rigid phenylsilsesquioxane (PSSO) blocks.

It is convenient to synthesize such copolymers using hydrolytic polycondensation, which implies that the formation of rigid phenylsilsesquioxane blocks occurs simultaneously with that of the bulk copolymer.[2,3] A salient feature of BC prepared in this manner is the presence of residual SiOH functional groups in the PSSO blocks. High reactivity of these groups allows ready chemical modification of the structure of the rigid blocks as well as the formation of additional chemical cross-links between the macromolecules, thus constructing a specific three-dimensional network structure.

Currently, particular attention is paid to the synthesis of polymer networks with bimodal chain length distribution of linear fragments between junctions, since the combination of long and short chains makes it possible to vary the strain-strength properties of the networks over a wide range.[4] In this connection, it was of interest to use the above-mentioned procedure for the preparation of siloxane BC with bimodal chain length distribution of flexible DMS blocks. The aim of this work was to synthesize and characterize a number of soluble phenyldimethylsiloxane BC belonging to this type of block copolymers, which can be considered as precursors for the synthesis of three-dimensional cross-linked networks.

Block copolymers were synthesized following the previously developed procedure[2] (Scheme 1).

Scheme 1



Linear DMS oligomers with the general formula **1** (R = Me) were binary blends of oligomers with bimodal molecular weight distribution. The conditions for the syntheses were chosen so that (i) the linear oligomers differed in average chain lengths by at least an order of

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Table 1. Properties of initial linear oligomers

n		M_n	M_w	M_w/M_n
prescribed	experiment			
20	25	1920	2325	1.40
200	210	15630	17040	1.39

Note. Oligomers with chains capped at both ends with trimethylsiloxy groups were studied.

magnitude; (ii) the mole fraction of the oligomer with smaller n was varied from 100 to 0 mol.% (these two values corresponded to unimodal BC); and (iii) the average compositions of the copolymers, determined as the Me_2SiO : $PhSiO_{1.5}$ molar ratio, were kept constant ($n : m$ = const).

Main characteristics of the linear DMS used in the syntheses are listed in Table 1. The ratio of short-chain and cyclic products in the oligomers was monitored by GLC. The fact that the actual molecular weights of the oligomers are somewhat greater than the prescribed ones can be explained by the equilibrium character of the polymerization of cyclosiloxanes.[5] This process is accompanied[6] by interchain exchange reactions, chain length redistribution, and the formation of weakly reactive, short-chain oligosiloxanolates stabilized by intramolecular association through the silanolate end groups (see Ref. 7).

The data listed in Table 1 were obtained by gel permeation chromatography (GPC) for oligomers with n = 20 and 200, whose chains were capped at both ends with trimethylsiloxy groups. These data correspond to linear DMS oligomers and do not take into account the presence of cyclosiloxanes, which are not involved in the formation of the copolymer chains in further stages of the synthesis. The polydispersities of the oligomers found in the real experiments (1.40 for the oligosiloxane with n = 20 and 1.39 for that with n = 200) characterize the distribution of the polymer (high-molecular-weight) fraction on the chromatograms of the corresponding oligomers.

The compositions and characteristics of the block copolymers synthesized following Scheme 1 were determined by ^{29}Si NMR spectroscopy and GPC. They are listed in Table 2. GPC data indicate that the products of hydrolytic polycondensation contain no homopolymers of DMS and PSSO. It should be noted that the study of a model hydrolysis reaction of phenyltrichlorosilane mixed with DMS oligomers capped at both ends with trimethylsiloxy groups and, hence, containing no functional end groups showed that no chain length redistribution occurs in the oligomers under the conditions of synthesis.

According to the results of X-ray diffraction, thermomechanical, and DSC studies, the BC obtained are two-phase systems with different degrees and morphology of microphase separation. The X-ray diffraction patterns of the BC display three halos with centers near $2\theta \approx 7.2°$, 12°, and 20° (Fig. 1). The positions of the first two halos are determined by the average intermolecular distances in the homopolymers of dimethylsiloxane and phenylsilsesquioxane (hereafter, PDMS and PPSSO, respectively). It should be noted that the halo near 7.2° appears as a weak, poorly resolved shoulder of the halo at 12°, especially for the BC-100 unimodal copolymer. This is likely due to incomplete segregation of the PPSSO phase and to the very small size of its domains. Qualitatively, the sizes of the microdomains of both phases in the BC can be judged from their turbidities. For instance, the BC-0 copolymer exhibits a rather intense opalescence, whereas the BC-100 copolymer is transparent. This indicates that the size of domains in the former copolymer is comparable with or longer than the wavelength of visible light, whereas for the latter copolymer this value is much shorter than the wavelength of visible light.

Qualitatively, the degree of segregation of DMS blocks to form a separate phase can also be judged from the results of DSC studies and thermomechanical analysis (TMA). The DSC curves of the rapidly cooled (64 deg min^{-1}) specimens of all BC (Fig. 2) indicate characteristic heat capacity increments near the glass transition temperature of PDMS (−125 °C). The degree

Table 2. Composition and characteristics of unimodal and bimodal block copolymers

Block co-polymer	Composition of block copolymers					Specifc viscosity, η	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n/\bar{M}_w$
	Linear block		Average block length		$n : m$ ratio				
	n = 20	n = 200							
	mol.%		n	m	(experiment)*				
BC-100	100	—	20	5	3.85	0.158	19116	30570	1.60
BC-98	98	2	24	6	4.03	0.088	28901	49891	1.73
BC-96	96	4	28	7	4.08	0.185	33767	57566	1.71
BC-92	92	8	36	9	3.86	0.244	42170	69391	1.65
BC-0	—	100	200	50	3.90	0.266	65734	67235	1.32

* Determined by ^{29}Si NMR spectroscopy; the prescribed $n : m$ ratio was 4 : 1.

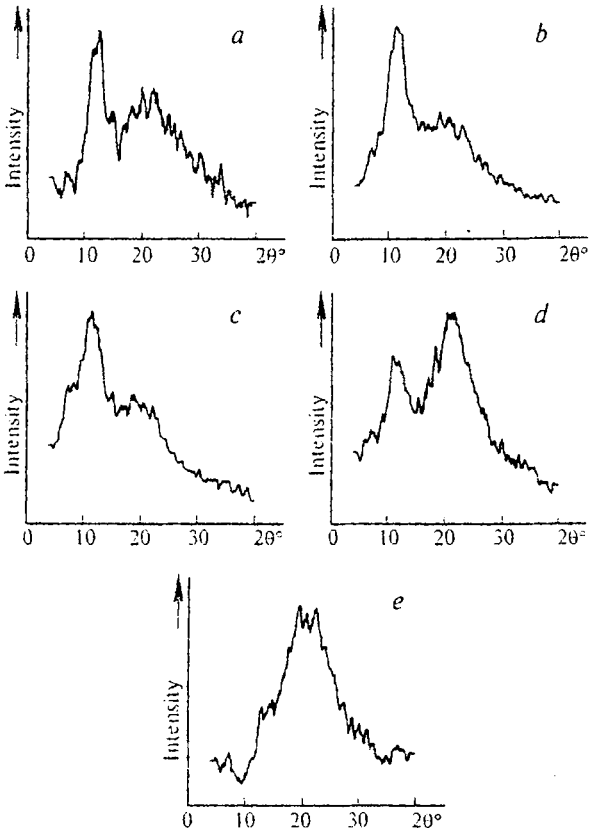

Fig. 1. X-ray diffraction patterns of block copolymers: BC-0 (*a*), BC-100 (*b*), BC-98 (*c*), BC-96 (*d*), and BC-92 (*e*).

of microphase separation in the BC-0 unimodal copolymer is high enough for the long DMS blocks to readily undergo crystallization. The DSC curves of this block copolymer also clearly indicate the melting of crystalline domains. Rapid preliminary cooling of the specimens allows observation of exothermic peaks of cold crystallization at temperatures near −100 °C, as is the case with high-molecular-weight homopolymers of DMS treated in the same manner. On the contrary, the DSC curve of a rapidly cooled BC-100 unimodal copolymer indicates only a heat capacity increment near T_g. The absence of the peaks of cold crystallization and subsequent melting of the PDMS phase is likely due both to the slow kinetics of the crystallization of short DMS fragments and to a lower degree of microphase separation. As to the bimodal BC and unimodal BC-100 block copolymer, both melting peaks and peaks of cold crystallization can be seen in the corresponding DSC curves.

The heats of melting of bimodal BC increase with increasing the fraction of long DMS blocks (see Table 3). It should be noted that even with a small mole fraction of DMS blocks with n = 200 in the DMS component of the block copolymers their weight fraction is rather high (0.17, 0.29, and 0.46 for the BC-98, BC-96, and BC-92 copolymers, respectively). This fact should be taken into account when analyzing the corresponding data.

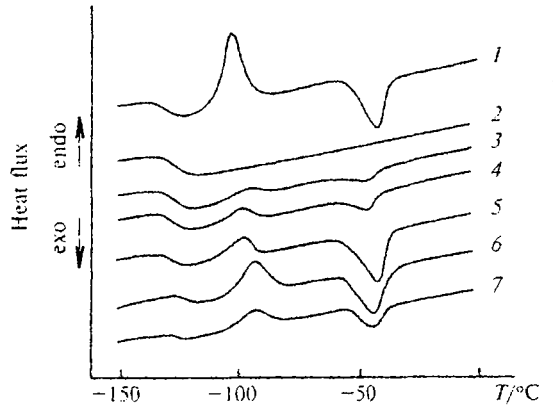

Fig. 2. DSC curves of unimodal and bimodal block copolymers and their blends: BC-0 (*1*), BC-100 (*2*), BC-98 (*3*), BC-96 (*4*), BC-92 (*5*), a blend of BC-100 and BC-0 copolymers taken in 98 : 2 (*6*) and 96 : 4 ratio (*7*). The heating rate is 8 deg min^{-1}.

It is known[8] that the degree of crystallinity of high-molecular-weight PDMS is nearly 50% and the heat of melting of the substance is 28 J g^{-1}. For the copolymer, this value is 27.3 J g^{-1} with respect to the PDMS phase. This means that a complete separation of the DMS and PSSO blocks occurs in the copolymer and that the size of the PDMS microdomains has no effect on the degree of crystallinity of the DMS blocks. The heats of melting of the BC-98 and BC-96 copolymers are nearly equal (4.7 J g^{-1} with respect to the PDMS phase). Based on the known fractions of the DMS blocks with n = 200 in the copolymers, the heat of PDMS melting (see above), and the assumption that these blocks form corresponding domains, we can say that for the BC-98 copolymer this value (4.7 J g^{-1}) formally corresponds to the heat of crystallization of the above-mentioned DMS blocks. As to the BC-96 copolymer, similar reasoning suggests that only 60% of the DMS blocks with n = 200 undergo crystallization. It should be noted that for each DMS block with n = 200 there are, on the average, nearly five macromolecules of BC-98 copolymer and three macromolecules of BC-96 copolymer (see the M_n values in Table 2). In the BC-92 copolymer, each macromolecule must, on the average, contain a long DMS block. In this case, a substantial increase in the heat of melting of the PDMS phase (up to ~24 J g^{-1} with respect to the PDMS phase) is observed, which indicates that DMS blocks with n = 20 are involved in the crystallization. Previously,[9] a similar phenomenon has been observed in studies on the crystallization of DMS oligomers containing small amounts of high-molecular-weight PDMS. This was explained by the crystallization of oligomeric molecules on nucleation centers formed by long macromolecules. Substantial increase in the heat of melting also implies the possibility of a greater separation of rigid and flexible blocks in this copolymer.

For comparison, Table 3 also lists the heat of melting of a blend of BC-100 and BC-0 copolymers taken in a

Table 3. Thermophysical properties of phase transitions in unimodal and bimodal block copolymers and in their blend

Block copolymer	T_{cr}/°C	Q_{cr} /J g^{-1}	T_m/°C	Q_m /J g^{-1}
BC-0	−108	16.7	−42	18.6
BC-98	−95	3.3	−48	3.3
			−56	
BC-96	−98	3.3	−47	3.3
			−55	
BC-92	−96	8.4	−42	16.7
			−49	
BC-100 + BC-0 (96 : 4)	−95	4.7	−44	5.5

Note. T_{cr} and Q_{cr} is the temperature and the heat of crystallization, respectively; T_m and Q_m is the melting point and the heat of melting, respectively.

0.96 : 0.04 molar ratio, which was prepared from a combined toluene solution. It should be noted that the solution become turbid even at the stage of removal of the solvent at high concentrations of the high-molecular-weight component, which indicated at least partial incompatibility of the two copolymers. The dried blend remained turbid and the heat of melting of the blend (7.9 J g^{-1} with respect to the PDMS phase) corresponded only to the crystallization of long DMS blocks in the BC-0 copolymer.

The ability of the PDMS domains to undergo crystallization determines the shape of TMA curves. For readily crystallizable BC-0, the TMA curve indicates almost no strain near the glass transition temperature of PDMS, whereas irrecoverable strain due to flow of the specimen is developed at temperatures above −40 °C after melting of the PDMS crystalline domains (Fig. 3, *a*). The TMA curve of unimodal BC-100 copolymer cooled at a rate of 5 deg min^{-1} indicates both a glass transition near −125 °C and flow of the specimen at temperatures above −40 °C, which means that DMS blocks with

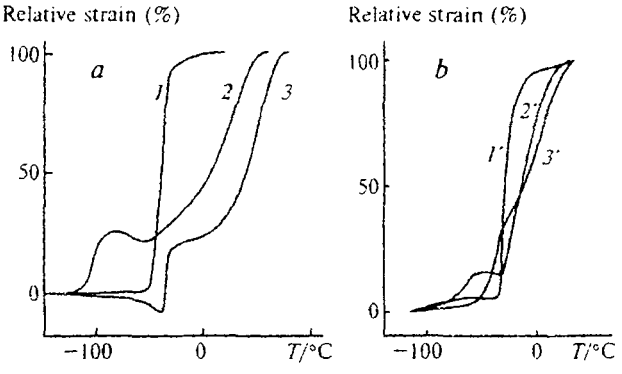

Fig. 3. TMA curves of unimodal (*a*) and bimodal (*b*) block copolymers obtained at a load of 0.1 MP for BC-0 (*1*), BC-100 (*2*), BC-96 (*1'*), BC-92 (*2'*), and BC-98 (*3'*) and at a load of 2 · 10^{-3} MPa for BC-20050 (*3*). The heating rate is 5 deg min^{-1}.

n = 20 also can to a small extent undergo crystallization on slow cooling. The TMA curves of bimodal BC characterized by a higher degree of crystallization than that of BC-100 copolymer indicate more pronounced glass transition and melting of the PDMS phase (see Fig. 3, *b*).

In essence, transition of unimodal and bimodal BC into the viscous-flow state at temperatures above the melting point of DMS blocks means that these blocks (their volume fraction in the copolymers is ~70%) form a nearly continuous matrix and that there are no strong physical junctions which link the siloxane chains to form a three-dimensional network. However, the situation reverses as the fraction of DMS blocks in the copolymer decreases. The PPSSO phase begins to play the role of matrix in the copolymer even if the volume fraction of DMS blocks decreases only by 4% (down to 66%), *i.e.*, at a DMS : PSSO block ratio of 20 : 6. This is confirmed by the fact that the TMA curves indicate no strain development in the temperature range corresponding to both glass transition and melting of the PDMS phase. It was found that the copolymer undergoes a transition from the glassy state into viscoelastic state at temperatures above 60 °C. The T_g value of the copolymer remains virtually unchanged as the fraction of phenylsilsesquioxane units increases. This effect can likely be explained assuming that for each length of DMS block there is a critical length of the PSSO block at which phase reversal occurs and that for DMS blocks with n = 20 this critical length equals 6.

Thus, the use of oligomers with bimodal molecular-weight distribution allows preparation of block copolymers with macromolecules with strongly different distances between rigid blocks, which leads to a greater degree of microphase separation of the blocks. We believe that polymer networks based on these bimodal copolymers containing both chemical joints and physical junctions will possess improved physicomechanical properties.

Experimental

GLC analyses were carried out on an LKhM-8 (Model 5) chromatograph (a 0.3×100 cm column, with 5% SE-30 on Chromaton N-AW-DMCS, with katharometer as detector, temperature programming in the range from 30 to 300 °C with a rate of temperature rise of 12 deg min^{-1}, and with helium as the carrier gas). GPC analysis was performed on a Waters instrument comprised of an M-600 pump, an M-410 refractometer, two Ultrastyragel 500 and 100 A columns, and a Maxima data acquisition system (conditions: chloroform as solvent, ~20 °C, solvent feed rate of 1 mL min^{-1}). Calibrations were performed against polystyrene standards.

Temperatures and the heats of melting were measured using a DSM-2M instrument in the temperature range between −150 and 70 °C. The temperature scan rate was 4.8 and 64 deg min^{-1}. Specimens of mass 10 to 20 mg were hermetically rolled in aluminum dishes. X-Ray diffraction studies were performed on a DRON-3 diffractometer (Cu-Kα radiation filtered with nickel foil) equipped with a temperature accessory in the temperature range −100 to 70 °C. TMA curves were recorded on a

Table 4. Compositions of the reaction systems used for the preparation of unimodal and bimodal block copolymers

Block co-polymer	Oligodiorganosiloxanes				Phenyltrichlorosilane	
	n = 20		n = 200		weight/g	number of moles
	weight/g	number of moles	weight/g	number of moles		
BC-100	10.0	0.0051	—	—	5.43	0.0255
BC-98	10.0	0.0051	1.63	0.00011	6.56	0.0310
BC-96	10.0	0.0051	3.40	0.00022	7.72	0.0365
BC-92	10.0	0.0051	6.53	0.00042	9.83	0.0465
BC-0	—	—	10.0	0.0006	6.74	0.0031

UIP-70M automated installation at a heating rate of 5 deg min^{-1} and at loads of 0.1 and 0.002 MPa.

Synthesis of block copolymers

Stage 1. Synthesis of oligodimethylsiloxanes. A 70% solution of hexamethylcyclotrisiloxane in toluene was placed into a flask equipped with a Dean—Stark trap and a calculated amount of 40% aqueous KOH was added at 70 °C. The reaction mass was stirred at 110—130 °C, the toluene—water azeotrope being distilled off. After 16 h, samples for GLC and GPC analyses and for NMR studies were taken. This stage resulted in oligomers capped at both ends with trimethylsiloxy groups. The properties of the oligomers are listed in Table 1.

Stage 2. Synthesis of 2,ω-(phenyldichloro)oligodimethylsiloxanes. Binary mixtures of potassium oligodimethylsiloxanolates were introduced into a 50% solution of phenyltrichlorosilane in toluene (phenyltrichlorosilane was taken in a six-fold excess; the Si—Cl : Si—OK ratio was 18 : 1) with vigorous stirring. Under these conditions, side reactions are completely suppressed. The ratios of the reagents used for the preparation of block copolymers of different composition are listed in Table 4.

Stage 3. Synthesis of block copolymers. The reaction mass obtained in stage 2 was rapidly introduced into a toluene—water mixture with vigorous stirring at 60 °C. After stirring the reaction mixture for an additional 0.5 h the toluene layer was separated from the aqueous layer and washed with water until disappearance of Cl^- ions. The characteristics of the block copolymers prepared are listed in Table 2.

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