Phase Morphology and Dynamic Mecahnical Properties of Model Polyblock Copolymers Prepared from Reactive Oligomers

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SUMMARY

Two polyblock copolymer (BCP) series of the type *(P/S)ₙ* (where *P* is the oligomeric azo-initiator and *S* is the styrene block) synthesized by sequential (series A) and simultaneous (series B) photo-initiated polymerization were characterized by small-angle X-ray scattering and by dynamic mechanical analysis. The molar mass characteristics of the BCP were little affected by methods of synthesis, whereas their morphologies and mechanical behaviour in the bulk state were widely different. Reasonably sharp SAXS peaks and distinct *log E′* falls concomitant to the glass-rubber transitions for the microphases of each chain component for samples of series B were regarded as evidence of a well-ordered, three-dimensional lattice of isolated *S* domains within a continuous *P* matrix. In contrast, the absence of well-defined SAXS peaks in the same range of scattering vectors combined with nearly two-fold smaller *log E′* falls at T_{gP} for samples of series A suggested the existence of two co-continuous, randomly interpenetrated microphases of *S* and *P* blocks with a broad distribution of microheterogeneities by size.

INTRODUCTION

Regular diblock and triblock copolymers belong to the family of thermoelastoplastics, in which the phase morphology (and hence, the mechanical properties) depend on the relative contents of the constituent, thermodynamically incompatible chain blocks[1,2]. Up till now, by far the largest portion of such block copolymers (BCP) has been produced by living polymerization of anionically reactive monomers (mostly, dienes for the soft block, and vinyls for the stiff block) which ensured a narrow molar mass distribution. The alternative method of BCP synthesis by chain-radical polymerization using oligomeric thermo- or photo-initiators has not been considered feasible in view of its low selectivity (hence, lower probability of block structure formation). However, a possible remedy to this deficiency may be the use of an oligomeric compound (macroinitiator MI) which would simultaneously serve as a soft fragment of a BCP, and also would initiate the radical polymerization of a vinyl comonomer[3-6]. This method seems more versatile, in so far as not only a well-characterized MI block is directly incorporated into the BCP chain, but the companion blocks can be prepared by different routes (i.e., either polymerization or polycondensation). Moreover, this would offer an opportunity to realize in full all the attractive features of a radical polymerization (e.g., a considerably weaker sensitivity to reaction conditions; a possibility of synthesis in water media; much wider choice of monomers, including those which can produce macroradicals only under the action of free radicals, such as vinyl chloride and/or vinyl acetate, etc.[5,6].

In a broad sense, an MI can be defined as a polymer or an oligomer with reactive (e.g., azo- and/or peroxy-) groups at chain ends, which are easily split to produce radicals for the initiation of polymerization of a comonomer to form another block of a BCP. In our previous papers[7-9], oligomeric MIs synthesized from a macro-diisocyanate (oligomer) and azo-compounds with the end functional groups were used both for thermal and for photo-initiation of polymerization of vinyl monomers. The latter method of reaction initiation turned out to be preferable due to the easier control of both the initiation rate (by changing the light intensity), and the growth rate and chain length of the second block (by changing the temperature).
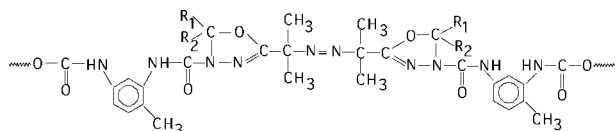
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N. A. Busko, V. K. Grishchenko, V. I. Shtompel, N. V. Babkina, V. F. Rosovitsky and V. P. Privalko

Thus, it is the purpose of the present paper to compare the phase morphology and mechanical properties of two BCP series, prepared by photo- and thermally initiated polymerizations.

EXPERIMENTAL

Materials

The oligomeric poly-azo-initiator (PAI) was synthesized from the prepolymer of toluene diisocyanate and random butadiene/isoprene copolymer (BIC; mass ratio: 80/20; molar mass: 4500 ±200; NCO content: 1.9%), and azo-*bis*-isobutyrohydrazone of cyclohexanone (AIC) as described in detail elsewhere[8]. The structure of PAI can be represented as - $(RX)_nR$, where R = BIC, and X is the initiator block shown below:

R_1 and R_2 are the alkyl radicals.

In so far as PAI formation through the reaction between the isocyanate groups of BIC and the hydrazone groups of AIC proceeds independently of the photo-initiated polymerization of styrene[9], it was possible to prepare two series of polyblock BCPs of the type *(P/S)_n* (where *P* is PAI, and *S* is the styrene block). The sequential one (series A) was obtained by the synthesis of PAI in the first step, and by subsequent radical polymerization of styrene photo-initiated by PAI, while both reactions were carried out in a single step to prepare the simultaneous one (series B). For comparison, one sample of series B was also synthesized by thermally-initiated radical polymerization.

As proved by exclusion chromatography (DuPont 8000, eluent: chloroform), for both BCP series, the major part of the reaction products was *(P/S)_n*, with traces of the recombination product of oligomeric rubber and styrene oligomer. The molar masses of *(P/S)_n* (Table 1) were calculated from the chromatograms using for calibration the model BCP specially prepared from macro-diisocyanate of BIC and oligostyrene dihydrazide (OSDH; molar mass: 8000 ±200). The mass ratios *P/S* of constituent blocks in the BCPs were

No	PAI/styrene (molar ratio)	$\langle M_n \rangle$	$\langle M_w \rangle$	$\langle M_z \rangle$	$\langle M_z \rangle/\langle M_n \rangle$	$\langle M_z \rangle/\langle M_w \rangle$	*P/S* ratio
Series A
1	1/143	12050 (23700)	24700 (37650)	38040 (41430)	2,05 (1,11)	1,54 (1,10)	45/41
2	1/200	12600 (27100)	21900 (29700)	30840 (32410)	1,74 (1,10)	1,41 (1,10)	45/49
3	1/400	10000 (31660)	27330 (35790)	38060 (39760)	2,73 (1,13)	1,39 (1,11)	45/82
Series B
1	1/143	14120 (26020)	26130 (28730)	46270 (31465)	1,85 (1,10)	1,77 (1,09)	45/42
2	1/200	15870 (27630)	43280 (42610)	89820 (82480)	2,73 (1,54)	2,08 (1,09)	45/49
3	1/300	16095 (37600)	45490 (46010)	78490 (80630)	2,56 (1,22)	1,58 (1,20)	45/58
4	1/400	12845 (36910)	30360 (73690)	80980 (138300)	2,36 (2,01)	2,67 (1,67)	45/88
5	1/400 (thermo)	16380 (119400)	41590 (164900)	149185 (208500)	2,54 (1,38)	3,58 (1,26)	45/498

Table 1 Molar mass characteristics of BCPs*#

* values in parenthesis were obtained from the integral areas under the first peaks on the chromatograms

$\langle M_n \rangle$, $\langle M_w \rangle$ and $\langle M_z \rangle$ are the number average, weight average, and Z-average molar masses

estimated by IR spectroscopy[10] (maximum error of the order of 10%). For calibration, the IR spectra of 5.5% carbon tetrachloride solutions of the PAI, of the OSDH and of their mixtures were recorded, and the intensity ratios of absorption bands at 1500 cm^{-1} (stretching vibrations of a monosubstituted benzene ring) and at 1550 cm^{-1} (bending vibrations of the NH bond) were plotted as a function of the PAI/OSDH ratio.

In view of the high initiating activity of AIC, it could be expected that the initiation rates of *S* polymerization would be higher (hence, the molar masses of *S* blocks would be lower) in samples of series B; however, the molar mass characteristics of the BCP of both series turned out to be little affected by the method of synthesis (Table 1). In a striking contrast to other samples of series B, the thermally-polymerized sample 5 of series B consisted, predominantly, of uninterrupted *S* blocks (Table 1).

Thin films of BCP for physical characterization were obtained by casting from chloroform solutions onto glass plates followed by subsequent evacuation overnight to a constant weight.

Methods

Dynamic Young's moduli E' were measured in the temperature interval from –130 to 100° C at a single frequency (about 100 Hz) with a custom-made Rheovibron-type DMA instrument[11, 12] at a constant heating rate of about 3 deg/min.
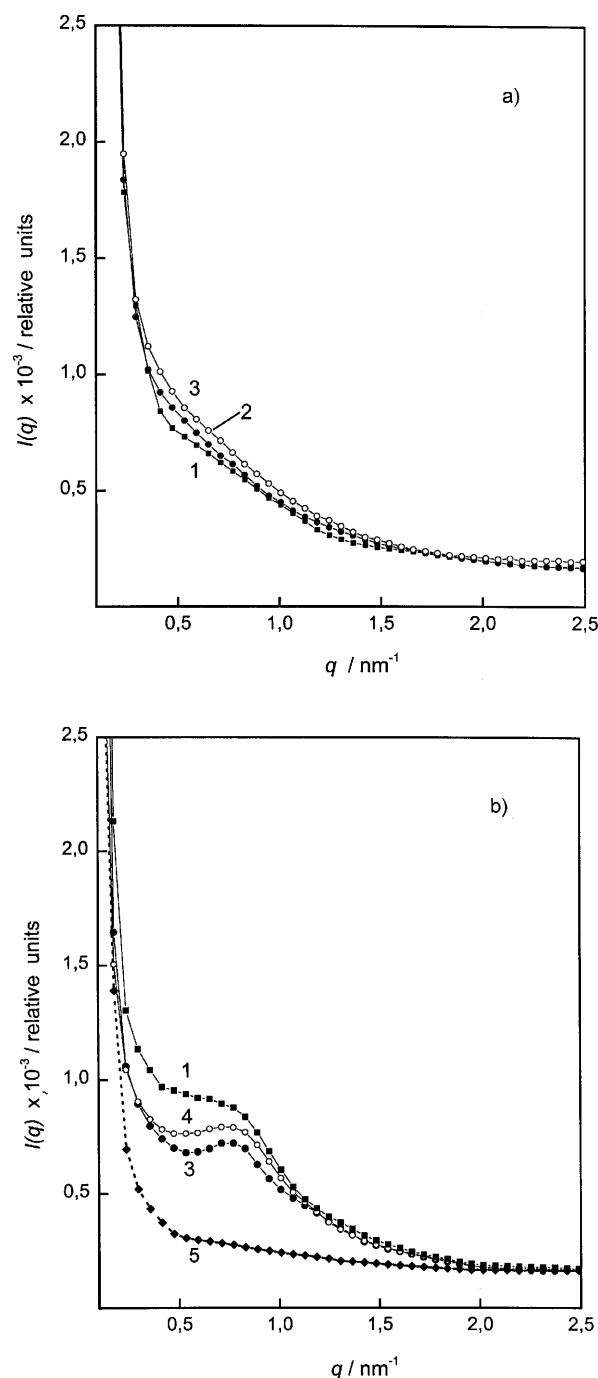
Small-angle X-ray scattering (SAXS) data were obtained with the Kratky camera (KRM-type diffractometer). The primary beam intensity was controlled with a monitoring channel in the scattering angle range from 3' to 5 deg ($2Q$). Copper K$_a$ radiation and nickel filtering of the primary beam were used. Recording of the scattering radiation with a scintillation counter and digital conversion were performed using the step-by-step scanning regime. The geometrical parameters of the X-ray beam in the specimen plane and the detector position (30 mm for the length of the homogeneous portion of the X-ray beam, and 290 mm for the specimen-detector distance) were chosen so as to satisfy the conditions of an "infinite" slit collimation[13].

RESULTS AND DISCUSSION

A common feature of the SAXS patterns for both the BCP series (except the thermally-polymerized sample

5 of series B) is the relatively high scattering intensity in the range of the scattering vectors $0.3 < q < 2.0$ nm^{-1} (Figure 1) which is characteristic of heterogeneous, microphase-separated systems. Reasonably sharp SAXS peaks around $q = 0.8$ nm^{-1} for samples of series B (Figure 1b) may be regarded as experimental

Figure 1 SAXS curves for samples of series A (a) and series B (b). Numbers correspond to the entries in Table 1: 1 (■), 2 (O) and 3 (●) in (a), and 1 (■), 3 (●), 4 (O) and 5 (♦) in (b)

N. A. Busko, V. K. Grishchenko, V. I. Shtompel, N. V. Babkina, V. F. Rosovitsky and V. P. Privalko

evidence for a well-ordered, three-dimensional lattice of isolated *S* domains within a continuous *P* matrix. In contrast, the absence of well-defined SAXS peaks in the same range of scattering vectors for samples of series A (Figure 1a) suggests a broad distribution of microheterogeneities by size, which may be tentatively attributed to the existence of two co-continuous, randomly interpenetrated microphases of *S* and *P* blocks. The complete absence of SAXS heterogeneity for sample 5 of series B (Figure 1b) can be regarded as evidence of a continuous macroscopic phase of uninterrupted *S* blocks with a few very small, randomly distributed inclusions of *P* blocks.
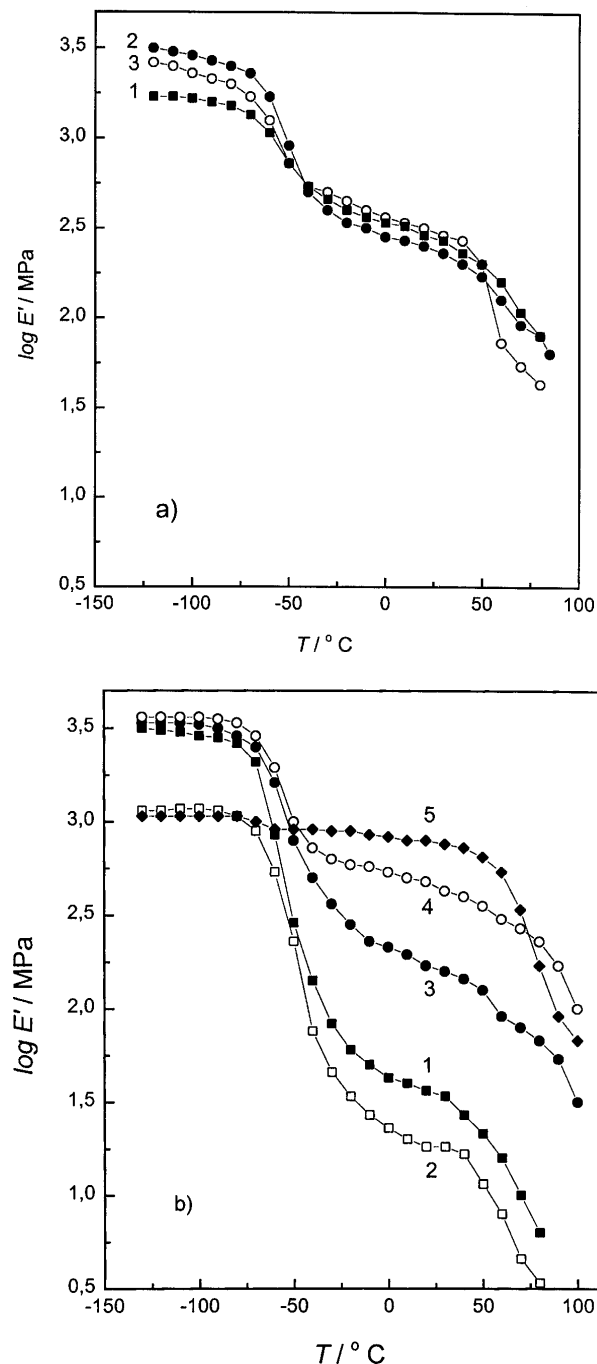
Similar conclusions can be reached from the analysis of *log E'* vs. *T* plots (Figure 2). In fact, the occurrence of distinct *E'* falls concomitant to the glass-rubber transitions for microphases of each chain component (in the temperature intervals $T_{gP} = -60\ (\pm 15)$ °C and $T_{gS} = 60°\ (\pm 15)$ °C for *P* and *S* microphases, respectively) for both BCP series is characteristic for microphase-separated systems. Moreover, the precipitous fall in *E'* by two orders of magnitude around T_{gP} for samples 1 and 2 of series B (Figure 2b) is exactly what one would have expected for a continuous soft *P* medium with isolated stiff S inclusions. In contrast, a nearly two-fold smaller *log E'* drop at T_{gP} for samples of series A (Figure 2a) is clear evidence of the reinforcement of the continuous *P* microphase by the co-continuous *S* microphase. This conclusion (i.e., absence of, or presence of a co-continuity of both microphases for samples 1 and 2 of series B, or for all samples of series A, respectively) is consistent with the widely different magnitudes of *log E'* falls around T_{gS} (Figure 2).

Apparently, similar morphological implications can be also invoked to explain both the SAXS patterns (Figure 1b) and the *log E'* vs. *T* plots (Figure 2b) for the remaining samples of series B. In particular, the persistence of high values of *log E'* over the broad temperature interval up to T_{gS} (with only a small inflection at T_{gP}) for sample 5 is consistent with the above morphological evidence for a continuous macroscopic phase of uninterrupted *S* blocks with a few very small, randomly distributed inclusions of *P* blocks.

CONCLUSIONS

The molar mass characteristics of two BCP series of the *(P/S)$_n$* type (where *P* is the oligomeric azo-initiator and *S* is the styrene block) turned out to be little affected by the method of photo-initiated synthesis

Figure 2 *log E'* vs. *T* plots for samples of series A (a) and series B (b). Numbers correspond to the entries in Table 1: 1 (■), 2 (O) and 3 (●) in (a), and 1 (■), 2 (❑), 3 (●), 4 (O) and 5 (◆) in (b)

(sequential and simultaneous for series A and B, respectively), whereas their morphologies and mechanical behaviour in the bulk state were widely different. Reasonably sharp SAXS peaks and distinct

$log E'$ falls concomitant to the glass-rubber transitions for microphases of each chain component for samples of series B were regarded as evidence for a well-ordered, three-dimensional lattice of isolated *S* domains within a continuous *P* matrix. In contrast, the absence of well-defined SAXS peaks in the same range of scattering vectors combined with nearly two-fold smaller $log E'$ falls at T_{gP} for samples of series A suggested the existence of two co-continuous, randomly interpenetrated microphases of *S* and *P* blocks, with a broad distribution of microheterogeneities by size.

ACKNOWLEDGEMENT

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