SYNTHESIS AND GAS PERMEABILITY OF BLOCK COPOLYMERS COMPOSED OF POLY(STYRENE-*co*-ACRYLONITRILE) AND POLYSTYRENE BLOCKS[+]

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Radical copolymerization of a mixture of styrene (S) and acrylonitrile (AN) at azeotropic composition (63 mole % of S and 37 mole % of AN) at 125 °C in the presence of dibenzoyl peroxide and 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) gave TEMPO-terminated S–AN copolymers with narrow molecular weight distributions. Both the linear semilogarithmic time–conversion and molecular weight–conversion dependences indicated a quasiliving copolymerization process. Polymerization of styrene initiated with the synthesized macroinitiators containing reversibly bound terminal TEMPO groups yielded film-forming poly(styrene-*co*-acrylonitrile)-*block*-polystyrene copolymers. Using the resulting diblock copolymer as a macroinitiator in copolymerization of S and AN, a triblock copolymer of the A–B–A type was obtained. Films of the block copolymers were prepared by casting chloroform solutions and their permeabilities (P) to nitrogen, oxygen, methane, carbon dioxide, and hydrogen were determined. The films showed high selectivities to oxygen ($P_{O_2}/P_{N_2} > 6$). The block copolymers behaved as single-phase homogeneous materials.

Keywords: Azeotropic styrene–acrylonitrile copolymers; Block copolymers; Nitroxide-mediated copolymerization; Gas transport; Radical polymerizations; Polymer films.

Block copolymers are important synthetic polymer products with broad practical utility. They can be used as thermoplastic elastomers, toughened thermoplastic resins, surfactants, membranes, and components of polymer blends[1]. Living chain-growth polymerization systems with anionic, cationic, group-transfer and Ziegler–Natta initiators and catalysts have been applied to the synthesis of such polymers[2]; however, the reagent purity is often restrictive and the variety of monomers polymerizable in this manner

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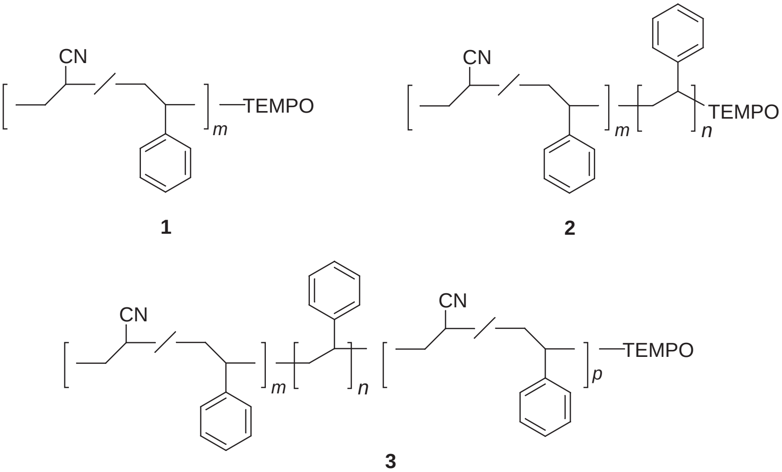
is rather limited. Some methods have been developed to obtain block copolymers also by radical polymerization, such as those using macroinitiators, multifunctional initiators or iniferters[3]. A great variety of block copolymers can be produced by condensation and coupling reactions[4]. However, depending on experimental conditions, problems appear with regard to their structure, low polydispersity and formation of homopolymers.

A renewed interest in the field of block copolymers has arisen due to the development of new radical polymerization techniques, affording polymers with controlled architectures and properties. Among other methods, nitroxide-mediated radical polymerization permits preparation of a wide range of different materials[5–31]. This approach involves addition of a nitroxide to a conventional polymerization system consisting of monomer and a typical thermal initiator, such as dibenzoyl peroxide or 2,2′-azobis(isobutyronitrile), in order to prevent irreversible bimolecular termination of macroradicals and to provide polymer chains with reversibly bound nitroxide end groups. The presence of the latter groups in the polymer chains opens the way to complex architectures such as block copolymers.

Recently, new diblock copolymers comprising random copolymer blocks were described by Fukuda *et al.*[14] Such block copolymers are interesting materials, whose properties can be extensively modified by changing the composition of comonomers and blocks. For example, through copolymerization of an azeotropic mixture of styrene and acrylonitrile in the presence of TEMPO-terminated polystyrene, polystyrene-*block*-poly(styrene-*co*-acrylonitrile) block copolymers were prepared and characterized. Also in other studies[32,33], the same procedure, *i.e.*, the copolymerization of styrene and acrylonitrile with a nitroxide-terminated polystyrene as a macroinitiator, was used for the synthesis of the above-mentioned diblock copolymers.

The aim of our work was to prepare film-forming block copolymers composed of poly(styrene-*co*-acrylonitrile) and polystyrene and evaluate their gas transport properties. First, in contrast to previous reports[14,32,33], TEMPO-terminated azeotropic styrene–acrylonitrile copolymers **1** were synthesized (Scheme 1), which served as precursors for poly(styrene-*co*-acrylonitrile)-*block*-polystyrene diblock copolymers **2**. Using the obtained diblock copolymer as a macroinitiator in the azeotropic styrene–acrylonitrile copolymerization, a triblock copolymer **3** of the A–B–A type was produced. The permeabilities to nitrogen, oxygen, methane, carbon dioxide, and hydrogen of the block copolymers were determined and the corresponding selectivities were calculated. On the basis of the published findings concerning the gas transport in binary polymer systems[34–37], morphology of the synthesized copolymers was also evaluated.



SCHEME 1

EXPERIMENTAL

Materials

Styrene (Kaučuk Group Co., Kralupy, Czech Republic) (b.p. 36 °C/1.56 kPa) and acrylonitrile (Fluka) (b.p. 78 °C/101.2 kPa) were distilled prior to use. The TEMPO radical (2,2,6,6-tetramethylpiperidin-1-yloxyl) (m.p. 36–39 °C) was a commercial product of Fluka. Dibenzoyl peroxide (Fluka) was reprecipitated from chloroform solutions with methanol. The solvents used were of analytical grade.

Synthesis of TEMPO-Terminated Azeotropic Styrene–Acrylonitrile Copolymers

An azeotropic mixture of styrene (S; $3.70 \cdot 10^{-2}$ mol, 63 mole %) and acrylonitrile (AN; $2.17 \cdot 10^{-2}$ mol, 37 mole %) containing dibenzoyl peroxide ($0.5 \cdot 10^{-4}$ mol) and TEMPO ($0.75 \cdot 10^{-4}$ mol) was heated at 125 °C in a sealed glass ampoule in an inert atmosphere for 1, 2, 2.5 or 3 h. The resulting TEMPO-terminated S–AN copolymer was precipitated from the reaction mixture and reprecipitated with methanol. It was dried under vacuum (6.7 Pa) at room temperature. The reaction conditions, conversions, molecular weights and their distributions (MWD) for the obtained azeotropic copolymers **1-1**–**1-4** are given in Table I.

Synthesis of Poly(styrene-*co*-acrylonitrile)-*block*-polystyrene

A solution containing 0.2 g of copolymer **1-1**, **1-2**, **1-3** or **1-4** (Table I) and 5 ml of styrene was heated in a sealed glass ampoule in an inert atmosphere at 125 °C. In the case of copolymer **1-3**, the polymerization using 0.3 g of this precursor and 7.5 ml of styrene was also carried out. After a predetermined time, the reaction mixture was poured into a ten-fold excess of methanol. The obtained polymer was reprecipitated from a chloroform solution with methanol and dried under vacuum (6.7 Pa) at room temperature. Table II summarizes the yields and some characteristics of the synthesized diblock copolymers.

Synthesis of Poly(styrene-*co*-acrylonitrile)-*block*-polystyrene-*block*-poly(styrene-*co*-acrylonitrile)

Copolymerization of an azeotropic mixture of S (4.24 ml, 63 mole %) and AN (1.44 ml, 37 mole %) in the presence of diblock copolymer **2-3** (0.2 g) at 125 °C for 0.5 h yielded triblock copolymer **3** (Table II).

TABLE I
Synthesis and properties of TEMPO-terminated azeotropic styrene–acrylonitrile copolymers[a]

Copolymer	Time, h	Yield, %	$M_n \cdot 10^{-4}$ [b]	M_w/M_n
1-1	1	7.4	1.38	1.17
1-2	2	21.0	2.12	1.16
1-3	2.5	36.3	3.78	1.23
1-4	3	41.4	4.05	1.18

[a] By copolymerization of azeotropic mixtures containing $3.70 \cdot 10^{-2}$ mol (63 mole %) of styrene, $2.17 \cdot 10^{-2}$ mol (37 mole %) of acrylonitrile, $0.5 \cdot 10^{4}$ mol of dibenzoyl peroxide, and $0.75 \cdot 10^{-4}$ mol of TEMPO at 125 °C. [b] Polystyrene-equivalent, SEC.

TABLE II
Synthesis and properties of block copolymers with poly(styrene-*co*-acrylonitrile) and polystyrene blocks[a]

Block copolymer	Polymer precursor[b]	Time, h	Yield, %	PS block[c] wt.%	$M_n \cdot 10^{-4}$ [d]	M_w/M_n
2-1	**1-1**	1	0.86	75.9	4.19	1.31
2-2	**1-2**	1	0.71	72.8	6.05	1.59
2-21	**1-2**	0.5	0.41	59.0	3.68	1.46
2-3	**1-3**	1	0.67	74.7	10.40	1.55
2-31[e]	**1-3**	0.5	0.68	60.0	8.34	1.45
2-4	**1-4**	1	0.69	71.9	10.41	1.50
2-41	**1-4**	0.5	0.41	59.1	8.56	1.47
3[f]	**2-3**	0.5	0.74	17.5	20.28	1.66

[a] By polymerization of styrene (5 ml) using 0.2 g of a polymer precursor at 125 °C. [b] See Table I. [c] From elemental analysis. [d] Polystyrene-equivalent, SEC. [e] 7.5 ml of styrene, 0.3 g of polymer precursor. [f] By azeotropic copolymerization of 4.24 ml (63 mole %) of styrene, 1.44 ml (37 mole %) of acrylonitrile, and 0.2 g of polymer precursor.

Preparation of Polymer Films

Polymer films with a thickness of 28–65 μm were obtained by casting chloroform solutions of copolymers (*ca* 0.1 g l^{-1}) on a glass plate to form a 0.35-mm layer and subsequent solvent evaporation at room temperature. They were dried under vacuum (6.7 Pa) for two days to remove the solvent residues.

Methods

The yields of copolymers were determined gravimetrically; their compositions were found from elemental analyses.

For evaluation of number- and weight-average molecular weights (M_n and M_w), the size-exclusion chromatography (SEC) measurements were carried out on a PSS SDV 10000 column (8 × 600 mm, Polymer Standard Service, Germany), filled with 5-μm sorbent particles. Tetrahydrofuran, distilled and dried over molecular sieves (4 Å), served as a mobile phase. Chromatographic data from refractometric and UV (254 nm) detectors were treated using the DataMonitor system (Watrex, Czech Republic). A universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used for determination of the molecular weights.

Gas transport properties of the films were studied using a laboratory high-vacuum apparatus with a static permeation cell. The polymer film was placed and sealed in a module, which was evacuated at 40 °C to degas the sample. At the beginning of a permeation experiment, the used gas under constant pressure, p_i (120–220 kPa), was introduced into the feed part of the permeation cell. The permeability, P, was determined from the increase in the pressure, Δp_p, in the calibrated volume of the product part of the cell, V_p, per time unit, Δt, during the steady-state permeation and calculated from Eq. (*1*):

$$\mathrm{P} = \Delta p_p/\Delta t \times V_p\ l/S\ p_i \times 1/RT\ , \qquad (1)$$

where l, S, R and T are the film thickness, film area, the gas constant and temperature, respectively. All the measurements were carried out at 30 °C.

Selectivities α were expressed in terms of the ratio of the corresponding permeabilities.

RESULTS AND DISCUSSION

TEMPO-Terminated Azeotropic Styrene–Acrylonitrile Copolymers

Table I presents the results on copolymerization of S and AN initiated with dibenzoyl peroxide in the presence of TEMPO. All the initial mixtures contained 63 mole % of S and 37 mole % of AN, *i.e.*, they had azeotropic composition[14]. Within the range of times 1–3 h at 125 °C, the conversions and molecular weights of resulting copolymers increased respectively from 7.4% and $1.38 \cdot 10^4$ up to 41.4% and $4.05 \cdot 10^4$. The mole fraction of the incorporated comonomers was approximately the same as that in the starting reaction mixtures. Similarly to the nitroxide-mediated homopolymerization of styrene[5,7], the obtained azeotropic TEMPO-terminated S–AN copolymers showed a very narrow MWD (M_w/M_n = 1.16–1.23).

As can be seen in Figs 1 and 2, the semilogarithmic time–conversion and molecular weight–conversion dependences for the S–AN copolymerization in the presence of TEMPO are linear. The shift of the line from the zero onset on the time axis in the former dependence reveals an inhibition at the beginning of the process; in this period (about 45 min), TEMPO radicals are obviously consumed under formation of potentially active initiating centers.

In accordance with the literature[7], the observed linear plots and low M_w/M_n values corroborated a quasiliving nature of the process with participation of TEMPO radicals, which reversibly terminate polymer chains. Under the experimental conditions, the rate of copolymerization, R_c, can be expressed by Eqs (*2*) and (*3*):

$$R_c = -\mathrm{d}[\mathrm{S + AN}]/\mathrm{d}t = K_{app}[\mathrm{S + AN}] \tag{2}$$

$$K_{app} = k_p[\mathrm{C}^*] \, , \tag{3}$$

where [S + AN] and [C*] are respectively the total molar concentrations of comonomers and active (or potentially active) centers at time *t*, and k_p is the rate constant of propagation.

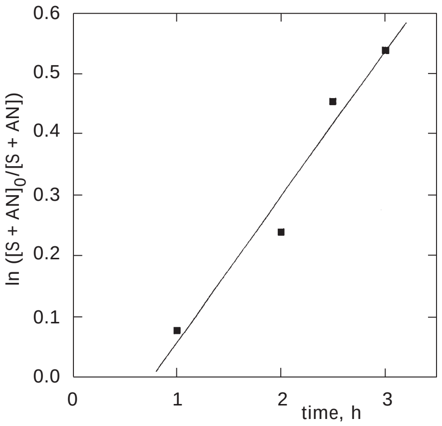


FIG. 1

The semilogarithmic time–conversion plot for azeotropic S–AN copolymerization in the presence of TEMPO (Table I). $[\mathrm{S + AN}]_0$ and [S + AN] are molar concentrations of the comonomers at the beginning and at a given time of the copolymerization, respectively

The [C*] is evidently constant in the course of the copolymerization under study.

Diblock and Triblock Copolymers with Poly(styrene-co-acrylonitrile) and Polystyrene Blocks

The synthesized TEMPO-terminated S–AN copolymers readily initiated polymerization of styrene at 125 °C (Table II). The resulting polymers showed several times higher molecular weights than the starting poly(S-*co*-AN) macroinitiators. As expected, after a 1-h polymerization with the same amounts of the macroinitiator (0.2 g), the shortest polymer chains were in copolymer **2-1** ($M_n = 4.19 \cdot 10^4$), prepared from **1-1** with the lowest molecular weight ($M_n = 1.38 \cdot 10^4$), while M_n of **2-4**, prepared from **1-4** ($M_n = 4.05 \cdot 10^4$), was equal to $10.41 \cdot 10^4$; this difference is due to a higher number of initiating centers in the former case. The determined molecular weights, yields, and the observed unimodal SEC curves of the products indicated the formation of poly(styrene-*co*-acrylonitrile)-*block*-polystyrene diblock copolymers. A broader MWD of the diblock copolymers than that of the precursors can be associated with both the side reactions deactivating quasiliving polymer chains[24–26] and a spontaneous thermal polymerization of styrene proceeding to some extent[7]. Nevertheless, considering similar weight fractions of polystyrene blocks generated after a 0.5-h (about 59 wt.%) or 1-h (about 74 wt.%) polymerization, approximately the same initi-

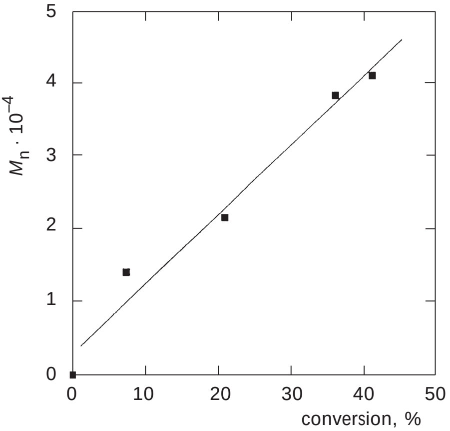


FIG. 2
The M_n–conversion plot for azeotropic S–AN copolymerization in the presence of TEMPO (Table I)

ation efficiency of the individual S–AN copolymer macroinitiators can be assumed.

A shorter reaction time led to diblock copolymers having lower molecular weights (*cf*. **2-2**, **2-21** and **2-4**, **2-41**). This demonstrates a quasiliving growth of polystyrene on polymer chains of the precursor.

The diblock copolymer **2-3** was used to initiate copolymerization of an azeotropic mixture of S and AN. During 0.5 h at 125 °C, triblock copolymer **3** with approximately double molecular weight than that of **2-3** was obtained. The formation of an additional block consisting of the azeotropic S–AN copolymer was confirmed by elemental analysis; the corresponding SEC curve indicated complete consumption of **2-3**. In comparison with **2-3** (M_w/M_n = 1.55), the MWD of **3** broadened (M_w/M_n = 1.66) owing to the presence of some inactive polymer chains of the macroinitiator contaminating the resulting triblock copolymer.

For illustration, Fig. 3 shows SEC curves for the azeotropic (**1-3**), diblock (**2-3**), and triblock (**3**) copolymers.

Gas Transport and Morphology

The synthesized copolymers provided homogeneous transparent films. However, only the films of copolymers with molecular weight higher than $4.2 \cdot 10^4$ were tough and mechanically resistant. The gas transport through the films of **2-2**, **2-3**, **2-4**, and **3** was measured and their selectivities were calculated (Table III).

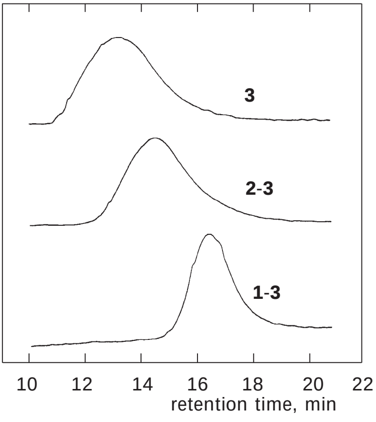


FIG. 3
SEC curves for the azeotropic (**1-3**), diblock (**2-3**), and triblock (**3**) copolymers

The diblock copolymers **2-2**, **2-3**, and **2-4** showed very close permeability values for all the used gases. Though differing in molecular weights, they contained approximately the same weight fractions of polystyrene (about 74 wt.%). Introduction of additional poly(S-*co*-AN) blocks in the chains (triblock copolymer **3**) caused a distinct decrease in permeabilities as compared with those of the precursor (**2-3**). As expected, the weight fraction of polystyrene in **3** decreased (below 18 wt.%), and, hence, the fraction of nitrile groups increased. All the copolymers composed of poly(S-*co*-AN) and polystyrene exhibited surprisingly high selectivities to oxygen ($\alpha_{O_2/N_2} > 6$).

The gas transport through polymers is essentially determined by their morphology. According to the literature[34–37], morphology of multicomponent polymer systems can be investigated using penetrating gas molecules. Diffusion of small molecules through polymers is very sensitive to the chain arrangement[34]. In a phase-separated binary system, the gas or vapour permeability is controlled by the prevailing component. At a certain threshold composition, a permeability jump can be observed[35]. However, in the case of a homogeneous binary system, the permeability P for a given gas approaches the weighted geometric mean of permeabilities P_1, P_2 for the components 1 and 2, as shown in Eq. (*4*):

TABLE III

Gas transport characteristics of block copolymers with poly(styrene-*co*-acrylonitrile) and polystyrene blocks

Gas transport characteristic[a]	Block copolymer[b]			
	2-2	**2-3**	**2-4**	**3**
P_{N_2}	0.29	0.29	0.36	0.16
P_{O_2}	1.83	1.79	2.18	1.01
P_{CH_4}	0.38	0.38	0.51	0.24
P_{CO_2}	8.20	8.38	10.2	4.41
P_{H_2}	19.6	19.8	21.4	13.8
α_{O_2/N_2}	6.3	6.2	6.1	6.3
α_{CH_4/N_2}	1.3	1.3	1.4	1.5
α_{CO_2/O_2}	4.5	4.7	4.7	4.3

[a] P and α are the gas permeability (in barrers, *i.e.*, in 10^{-10} cm^3 (STP) cm/(cm^2 s cm Hg)) and selectivity (the ratio of the corresponding permeabilities), respectively. [b] See Table II.

$$\ln P = \phi_1 \times \ln P_1 \times \phi_2 \times \ln P_2 \,, \qquad (4)$$

where ϕ_1 and ϕ_2 are volume fractions of the components[36]. This behaviour was observed also for S–AN random copolymers[37], with a small positive deviation from Eq. (*4*).

The dependences of permeabilities of the synthesized diblock and triblock copolymers to oxygen and carbon dioxide on the volume fraction of polystyrene can be seen in Figs 4 and 5. The data for polystyrene were re-

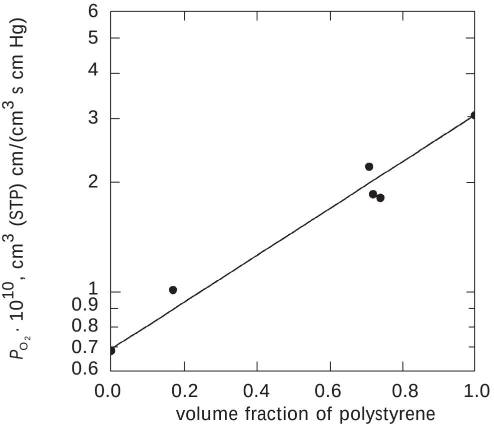


FIG. 4

Dependence of the permeability to oxygen on the volume fraction of polystyrene in poly(styrene-*co*-acrylonitrile)–polystyrene block copolymers

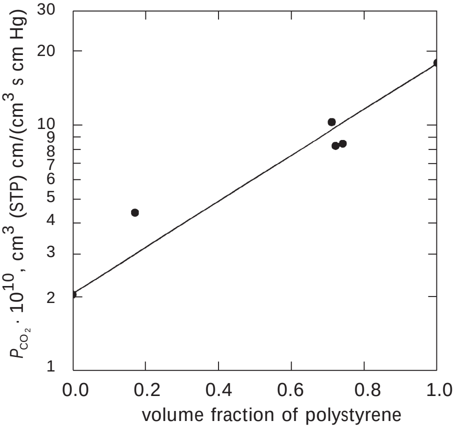


FIG. 5

Dependence of the permeability to carbon dioxide on the volume fraction of polystyrene in poly(styrene-*co*-acrylonitrile)–polystyrene block copolymers cently obtained in our laboratory, those for the azeotropic S–AN copolymers by interpolation of published values[36] for 25 °C using Eq. (*4*) and recalculating them with regard to a different temperature of measurements (30 °C). The found values for copolymers **2-2**, **2-3**, **2-4**, and **3** fit satisfactorily the line showing the weighted geometric mean of permeabilities of both polystyrene and S–AN copolymer. At the same time, no jump appeared. These results as well as transparency of the films indicate that the prepared block copolymers composed of poly(styrene-*co*-acrylonitrile) and polystyrene are homogeneous, single-phase materials.

CONCLUSIONS

TEMPO-mediated radical azeotropic copolymerization of S and AN at 125 °C initiated with dibenzoyl peroxide proceeded in a quasiliving manner yielding S–AN copolymers of narrow molecular weight distributions. They were used as precursors for the synthesis of film-forming poly(styrene-*co*-acrylonitrile)-*block*-polystyrene diblock copolymers. Copolymerization of an azeotropic S–AN mixture in the presence of the obtained diblock copolymer afforded a terpolymer with additional poly(styrene-*co*-acrylonitrile) blocks.

Films of the synthesized diblock and triblock copolymers were characterized by permeabilities to nitrogen, oxygen, methane, carbon dioxide, and hydrogen and by corresponding selectivities. A notable high selectivity to oxygen, $\alpha_{O_2/N_2} > 6$, was found for all the copolymers. The permeability measurements also revealed that the copolymers under study behaved as homogeneous binary systems.

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