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BLOCK COPOLYMERS POLYCAPROLACTAM–POLYSTYRENE–POLYCAPROLACTAM PREPARED BY THE ANIONIC POLYMERIZATION OF CAPROLACTAM

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Abstract—ABA block copolymers, where A and B represent polyamide and polystyrene segments respectively, were prepared by the anionic polymerization of caprolactam activated with polystyrene-*bis*-acyllactams. Under mild polymerization conditions (in a solvent at 120°), very pure copolymers were obtained containing only traces of polystyrene homopolymer and ≤ 2.5% of polycaprolactam. The length of the blocks A can be controlled by the polymerization time and by the amount and type of the solvent.

INTRODUCTION

In principle, block copolymers containing polyamide segments can be prepared by two routes, viz. by bonding prepolymers with reactive endgroups in condensation and addition reactions, or by building up the polyamide chain at the endgroups of the second prepolymer. The latter route has been employed several times in the preparation of block copolymers of the AB and ABA type, where A is the polyamide segment formed by the polymerization of lactam and B is another polymer segment. Both hydrolytic polymerization of lactams on the growth centres consisting of amino groups of prepolymer B [1, 2] and the anionic polymerization on active groups attached at one or both ends of the block B [3–7] were used. Polystyrene [4–6], polybutadiene [6], polydimethylsiloxane [3], polytetrahydrofuran [4] and a polyamide different from A [7] were used as blocks B. These prepolymers were terminated with N-acyllactam [3, 5, 7], chloroformate [4] or isocyanate [6] active groups, which acted as growth centres in the polymerization of caprolactam [3, 4, 6, 7], 2-pyrrolidone [4, 5] and dodecanelactam [3]. The polymerization conditions used by various authors differed considerably; the block copolymers (if they were characterized) contained major [6] or minor [4] fractions of the homopolymers A and B.

Compared with the hydrolytic polymerization, the use of the anionic polymerization of lactams in the preparation of block copolymers has considerable advantage in allowing lower polymerization temperatures and shorter times, when exchange reactions of the amide groups leading to the homopolymer A can still be neglected. The method just described is however not free of problems. Besides the limited choice of the prepolymer B, which must be stable and inert under the conditions of anionic polymerization, the main factors affecting the purity of the resulting copolymer are (a) the type of active endgroup of the prepolymer B, and (b) polymerization conditions with respect to side reactions.

It has not been the objective of this work to prepare a new polymeric material; we wanted to demonstrate that, taking into account the knowledge of the mechanism and side reactions of the anionic polymerization of lactams, conditions can be chosen such that the resulting copolymer is virtually free from homopolymers.

EXPERIMENTAL PART

Preparation of polystyrenes with active endgroups

4,4'-Azobis(4-cyanovaleric) acid was prepared by Strecker's synthesis [8] from levulinic acid (yield 24%, m.p. 112.5–123°-decomposition) and fractionated by extraction with 10% aqueous methanol into isomers differing in melting point [8]: 112–114° (isomer Ia) and 130–132° (water) (isomer Ib).

4,4'-Azobis(cyanovaleroyl) dichloride (II). Isomer Ia or Ib (1 g; 3.57 mmol) was dispersed in 5-15 ml dry CCl_4 (dried over molecular sieves 4A), and 1.5–1.6 g PCl_5 (7.20–7.68 mmol) was added at room temperature. The suspension was stirred at room temperature for 3 hr. During conversion into chloride, isomer Ia is dissolved while isomer Ib remains in suspension. After the solvent and $POCl_3$ had been removed *in vacuo* 130 Pa (5 hr, 25°), white or slightly yellow chloride was obtained, m.p. 74–82 and 82–5°, respectively.

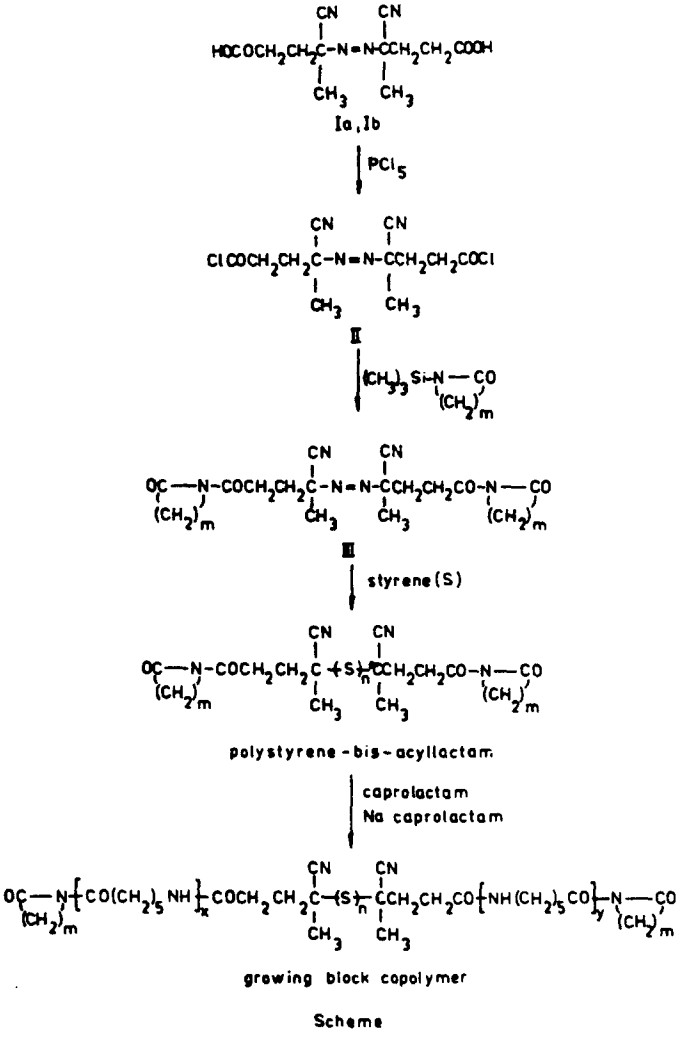
4,4'-Azobis-[*N*-(4-cyanovaleroyl)-ω-lactams] (III). Dichloride II (3.57 mmol) was dispersed in 5–15 ml dry CCl_4; the suspension was cooled to 0°, and 1 equivalent (7.14 mmol) of the respective *N*-trimethylsilyllactam [9] was added. The mixture stood overnight at 0°. After CCl_4 and trimethylchlorosilane had been evaporated *in vacuo* 130 Pa (25°), the products were either directly crystalline or oils which crystallized after trituration with methanol; the products were recrystallized from CH_2Cl_2–ether and are characterized as follows (see Scheme):

III ($m = 5$, from isomer Ia): yield 38%; m. p. 79–81° (decompn); for $C_{24}H_{34}O_4N_6$ (mol. wt. 470.6) calculated C 61.25, H 7.28, N 17.86%; found C 61.00, H 7.34, N 18.05%.

III ($m = 5$, from isomer Ib): yield 59%; m.p. 118–20° (decompn); found C 61.20, H 7.31, N 17.48%.

III ($m = 7$, from Ia): yield 86%, m.p. 76–79° (decompn); for $C_{28}H_{42}O_4N_6$ (mol. wt. 526.7) calculated C 63.85, H 8.04, N 15.96%; found C 63.78, H 8.08, N 16.19%.

III ($m = 7$, from Ib): yield 83%; m.p. 107–109° (decompn); found C 63.83, H 8.33, N 15.85%.



Scheme

III ($m = 11$, from Ia): no crystalline product was obtained.

III ($m = 11$, from Ib): yield 73%; m.p. 105–106° (decompn) for $C_{36}H_{58}O_4N_6$ (mol. wt. 638.8) calculated C 67.68, H 9.15, N 13.16%; found C 68.02, H 9.22, N 12.71%.

Styrene (Kaučuk, Kralupy) was distilled with calcium hydride at reduced pressure before polymerization. Polymerization was carried out in sealed ampoules under pure argon at 90° in dimethylformamide purified by rectification with benzene and water; the concentration of styrene was 4.09 mol l^{-1} and that of azo initiator 10–143 mmol l^{-1}; reaction continued for 18–50 hr up to conversions of 52–82%. Polystyrene was isolated and purified by precipitation into methanol, and dried at 25° and 130 Pa.

The concentration of the terminal acyllactam groups was determined from the absorbancy of the imide carbonyls in the i.r.; 2.5% solution of polystyrene in CCl_4 was measured in a NaCl cell (0.98 mm) against 2.5% solution of polystyrene (without endgroups prepared by anionic polymerization), in a compensation cell of adjustable thickness. The extinction coefficients $\epsilon = 873$ l/mol.cm at $\lambda_{max} = 5.88$ μm for acylcaprolactam and $\epsilon = 808$ l/mol.cm at $\lambda_{max} = 5.90$ μm for acyloctanelactam were determined from calibrations with solutions of the respective azo initiators in CCl_4. A Perkin–Elmer 457 spectrophotometer was used. The content of acyllactam groups was also determined from the amount of end lactams split off by aminolysis: 0.2 g polystyrene was heated in a sealed ampoule under argon with 4 ml toluene and 300% benzylamine (based on the expected concentration of acyllactams) at 50° for 100 hr; the solution was evaporated, the residue was digested with methanol containing benzophenone as the chromatographic standard, and the methanolic solution was analyzed in a 1 m column with 10% Carbowax 20M on Chromosorb W (80–100 mesh) at 170° and 50 ml min^{-1} nitrogen as carrier gas (Perkin–Elmer F11 chromatograph with flame-ionization detector).

The intrinsic viscosity of polystyrene was determined by extrapolation from three measurements in an Ubbelohde viscometer (toluene as solvent, 25°, concentration 0.8–1.6 g $dl.^{-1}$).

Anionic polymerization of caprolactam

Purification and drying of caprolactam, preparation of sodium caprolactam and of *N*-benzoylcaprolactam have been described (cf. Ref. [9, 10]). Toluene was dried by distillation with NaH; *N*,*N*-dimethylacetamide (Koch-Light) was rectified with benzene and dried over molecular sieves 5A. The initiator was dissolved in 3 g caprolactam in a flask with a Teflon coated magnetic stirrer, air reflux condenser and inlet and outlet for argon. To this solution, a solution of the polystyrene activator in a chosen volume of solvent was added at room temperature, and the mixture was heated with stirring at 120°. The polymerization was stopped by cooling and by transferring the reaction mixture into methanol. The copolymer was isolated by threefold extraction with boiling methanol (250 ml, 5 min) and dried at 50° and 130 Pa for 24 hr. Reference polymeriza-

tions with *N*-benzoylcaprolactam and polymerizations without solvent were carried out similarly.

NMR spectra of copolymers were recorded at 81° in 8% solution in the mixture trichloroacetic acid–tetrachloroethane (1:1 v/v) with a JEOL 100 spectrometer. The viscosities of copolymers were measured in tricresol at 25° and a concentration of 0.4 g dl.$^{-1}$ DTA measurements were performed with Du Pont Thermal Analyzer 900 at a heating rate 10° K min^{-1}. Soluble fractions for TLC were obtained by extracting with toluene in a Soxhlet extractor for 24 hr and by extracting of 0.2 g copolymer in 80% formic acid at room temperature for 24 hr. TLC was performed on glass plates 5 × 20 cm with a 0.1 mm layer of Kieselgel G (Merck).

RESULTS AND DISCUSSION

Polystyrenes with terminal *N*-acyllactam groups were used as prepolymer B (cf. Scheme). The acyllactam groups are chain growth centres in the anionic polymerization of lactams, so that the blocks A and B are connected by an amide group equivalent to the other amide groups of the block A. On the other hand, if polymeric activators are used with groups which are only precursors of the growth centres, the higher reactivity of the connecting group between the blocks may result in the formation of homopolymers. In earlier papers, this was the case for urea [6] and ester [4] bridges between the blocks.

Polystyrene terminated by growth centres (block B)

Polystyrene-*bis*-acyllactams (cf. Scheme) were prepared by radical polymerization of styrene using radical initiators, 4,4′-azobis-[*N*-(4-cyanovaleroyl)-ω-lactams] (III). A derivative of 2-pyrrolidone (m=3) was prepared for this purpose by Yamashita *et al.* [5] by reacting 4,4′-azobis(4-cyanovaleroyl) chloride with pyrrolidone in excess. To obtain derivatives of higher lactams in a higher yield, the process was modified. Crystalline products were obtained only if the acid was separated into higher- and lower-melting isomeric components, Ia and Ib, by an extraction method described by Haines and Waters [8], who called the two components the meso and racemate forms. The higher-melting isomer Ia could be transformed into chloride II by treatment with thionylchloride, only in the presence of DMF as catalyst, at temperature above 60°. Under such conditions the azo compounds are partly decomposed, so reducing the yields of bisacyllactams and makes more difficult their isolation in the crystalline form. Therefore, chloride II was better prepared at room temperature or lower by reaction with PCl_5 in CCl_4. Chloride II was best transformed into the respective acyllactam III by reaction with the respective *N*-trimethylsilyllactam [9]. The general description of this preparation is given and the azo initiators are specified in the Experimental Section. From two isomeric fractions of the acid, a pair of isomeric bisacyllactams is always formed, differing in physical properties. Only for dodecanelactam, the crystalline product III (m = 11) could not be prepared from the lower-melting fraction of acid Ia.

Polystyrene-*bis*-acyllactams were prepared under conditions best ensuring their telechelicity. Since termination of polystyrene occurs only by combination and under the given conditions transfer to polymer, monomer and solvent are unimportant [5], only bifunctional polystyrenes are formed. Monofunctional acyllactams can arise solely in side reactions of the terminal group, e.g. by hydrolysis or aminolysis with traces of water or amine present in the mixture, or by solvolysis during precipitation. However, the respective lactam could not be detected in the concentrated filtrate after reprecipitation of polystyrene from benzene solution into methanol (TLC and GLC). The constants of the Mark–Houwink equation were calculated from the intrinsic viscosities and concentrations of terminal acyllactam groups determined by i.r. spectroscopy and from the aminolytically split-off lactam assuming that both ends of the polystyrene chain consist of acyllactam groups (Table 1). For polystyrene-*bis*-acyllactams, it was found that $[\eta] = 4.43 \times 10^{-4}\bar{M}^{0.66}$. According to the intrinsic viscosity average molecular weights relationships for polystyrenes of similar $\bar{M}_w$, the $[\eta]$ values roughly correspond to values of $\bar{M}_n$ 2.5 to 3 times higher than those found by us. However, the parameters of the Mark–Houwink equation were always determined for narrow molecular weight distributions, i.e. for fractions [12–14] or polymers prepared by the "living" technique [15, 16], or they were determined for $\bar{M}_w$ (Ref. [17]); thus, our low $\bar{M}_n$ values indicate a comparatively broad distribution for our polymers. This is also suggested by very good agreement between our relationship and that found by Bamford and Dewar [18] for unfractionated polystyrenes in our range of $\bar{M}_n$: $[\eta] = 4.40 \times 10^{-4}\bar{M}_n^{0.65}$.

Table 1. Polystyrene-*bis*-acyllactams

No.	m	n	I*mol.kg^{-1}	$\bar{M}_n$†	$[\eta]$,‡ dl.g^{-1}
S 1	5	371	0.0513	39,080	
S 2	5	346	0.0549	36,476	0.431
S 3	5	181	0.104	19,292	0.305
S 4	5	174	0.108	18,563	
S 5	7	150	0.124	16,120	
S 6	5	146	0.129§	15,647	0.240
S 7	7	102	0.180	11,121	0.226
S 8	5	96	0.192‖	10,440	0.184
S 9	5	82	0.224	8982	0.173
S 10	5	81	0.227	8878	
S 11	7	71	0.254	7893	
S 12	7	69	0.260	7684	0.157
S 13	5	43.0	0.412	4921	0.108
S 14	7	40.5	0.427	4716	
S 15	7	38.2	0.447	4477	0.123

* Concentration of acyllactam from i.r. spectra.
† No. average molecular weight calculated from I.
‡ Toluene, 25°C.
§ Determined by aminolysis and GLC: 0.120 mol. kg^{-1}.
‖ Determined by aminolysis and GLC: 0.174 mol.kg^{-1}.

Polymerization

To eliminate side reactions, by which new growth centres and chains of homopolymer A are formed, we chose very mild conditions viz. 120°, and polymerization in the presence of solvent. The solvent made possible more rapid and better mixing of components at the start of polymerization, and allowed constant temperature to be maintained. The polymerization kinetics, and thus also the length of the segments A, are affected by the dissociation equilibrium of sodium

Table 2. Anionic polymerization of caprolactam with polystyrene activators. Caprolactam 3 g, sodium caprolactam 0.133 mmol, 120°C, solvent–toluene

No.	$\bar{P}_B$	I mmol	PhMe ml	t, hr	p %	wt.*	$\bar{P}_A$ NMR	N†	η_{sp}/c‡ dl.g^{-1}	M.p.,§ °C
C 1	43	0.144	10	1	3.4	7.0	11		0.213	none
C 2	43	0.143	10	6	14.9	27.8	26		0.908	215
C 3	146	0.129	10	1	3.2	7.4	8		0.249	199
C 4	81	0.131	10	6	15.2	30.9	30		1.008	222
C 5	174	0.130	10	6	17.8	36.1	35	35	0.995	213
C 6	174	0.129	10	24	15.7	32.3	30		1.126	213
C 7	81	0.130	5	6	26.5	53.7	53		1.680	223
C 8	43	0.142	0	6	97.0	182	—	160	7.12	222
C 9	43	0.143	10	1††	5.6	11.1	12		0.452	211
C 10	181	0.127	5**	1	28.9	60.0	68		1.061	223
C 11	‖	0.133	10	6	6.5	—			0.345	
C 12	‖	0.133	5**	1	20.1				0.342	

$\bar{P}_B$ and $\bar{P}_A$—no. average degrees of polymerization of polystyrene and polycaprolactam segments, resp. I—acyllactam concen.; t—polymerization time, p—yield of copolymer.

* Calculated from the weight increase of polymer.

† Calculated from the nitrogen content in copolymer.

‡ Measured in tricresol, 25°C, 0.4 g.dl^{-1}.

§ DTA endotherm at the heating rate 10°K.min^{-1}

‖ Activator *N*-benzoylcaprolactam.

** Polymerized in *N*,*N*-dimethylacetamide.

†† Polymerization bath temperature 140°C.

caprolactam and by the solubility of the copolymer in the given solvent–caprolactam system. At the same time, the polystyrene fraction of the growing copolymer also contributes to the change in polarity and in the solvent power of the polymerization mixture. The results in Table 2 indicate how the polymerization yield, and consequently the length of the segments A, can be controlled. With toluene as solvent, a conclusive role is played by the concentration of the polymerization mixture (series C4 < C7 < C8); a lesser effect is exerted by the polymerization time (series C1 < C2, C5 = C6). Precipitation of the copolymer from solution causes after some time the polymerization to be considerably slowed down. The polymerization rate increases on going from a nonpolar solvent (toluene, C6) to a polar one (*N*,*N*-dimethylacetamide, C10), due probably not only to an increase in the concentration of the lactam anions, but also to the delayed precipitation of the copolymer.

The delayed precipitation of the polymer also explains the higher yields obtained under comparable conditions in copolymerizations compared with homopolymerization (C2, C5 > C11; C10 > C12).

Properties and composition of block copolymers

Block copolymers prepared by solution polymerization are white powders or tough flakes. They are soluble at room temperature in cresols, in mixtures phenol–toluene (2:1), trichloroacetic acid–1,1,2,2-tetrachloroethane (1:1) and trichloroacetic acid–chloroform (1:1). They also dissolve at 100° in trifluoroacetic acid saturated with tetrachloromethane, in the mixture trichloroacetic acid–tetrachloroethylene (1:1) and partly in tetrachloroethane. They are insoluble in other solvents for polycaprolactam, such as formic, sulphuric, hydrochloric and trifluoroacetic acids, trifluoroethanol, dimethylformamide, benzyl alcohol and dimethylsulphoxide, and in the usual solvents for polystyrene.

Starting from a certain length of the blocks A, the copolymers exhibit a first-order transition region at a temperature identical with, or slightly lower than, that of the melting range of polycaprolactam. The temperatures corresponding to the endothermal maximum at DTA given in Table 2 show some dependence on the length of the blocks A. It should be noted, however, that the crystalline phase of the copolymers was formed during precipitation from solution during polymerization and that the copolymers were not subjected to further thermal treatment, e.g. annealing. This is also why the above temperatures do not correspond to an optimum arrangement of the chains A and to the equilibrium degree of crystallinity.

The number average degrees of polymerization of the blocks A ($\bar{P}_A$) for the assumed exclusive formation of the copolymer ABA were calculated from weight yields of the copolymers and from the ^{1}H NMR spectra of copolymer solutions. The calculation from the yield

$$\bar{P}_A = (\Delta g/113.16\, I) + 1$$

where Δg is the weight increment of isolated copolymer to the weight of the polystyrene activator used and I is the molar amount of the terminal acyllactam groups of activator, assumes complete utilization of the acyllactam groups as growth centres.

The NMR spectra of block copolymers were evaluated as by Yamashita [5] (cf. Fig. 1). The $\bar{P}_A$ values for the assumed ABA type of copolymer were calculated from the integrated areas of the peaks a and b, or a and $(b + c + d)$ using the relationships

$$\bar{P}_A = 5\bar{P}_B b/4a$$

$$\bar{P}_A = \bar{P}_B[5(b + c + d) - 3a]/20a.$$

Table 2 gives mainly averages from both calculations. For two copolymers, $\bar{P}_A$ values calculated from nitrogen content in copolymers are also given. The values were obtained from

$$\bar{P}_A = (56.032 - N\bar{M}_B)/(226.32N - 28.016).$$

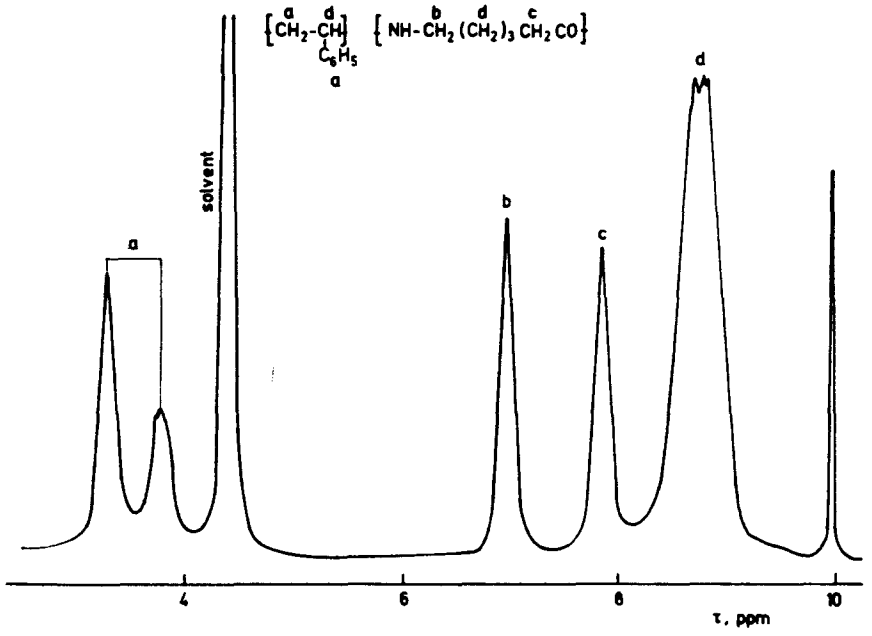


Fig. 1. ^{1}H NMR spectrum of the block copolymer styrene–caprolactam in the mixed solvent trichloroacetic acid–1,1,2,2-tetrachloroethane (100 MHz).

where N is the weight fraction of nitrogen in the copolymer, and $\overline{M}_B$ is the number average molecular weight of the polystyrene activator, including the incorporated residues of azo initiator. The good agreement between the $\overline{P}_A$ values confirms the reliability of gravimetric determination.

Homopolymer content

The presence of homopolymers in block copolymers containing polyamide segments was mainly investigated by selective extraction [4, 6] sometimes combined with fractional dissolution [6]. In our case, the copolymer was first isolated by extraction with methanol which does not dissolve homopolymers. The residue, insoluble in methanol, was then extracted with toluene. The amount of the toluene-soluble fraction depends on the ratio of $\overline{P}_A$ to $\overline{P}_B$ and was highest in the copolymer C6, viz. 8.5%. It was demonstrated, by TLC on silica gel, that the above fraction contains only traces of polystyrene and that it almost exclusively consists of the copolymer fraction richer in styrene. In developing with chloroform, R_F of polystyrene is 0.9–1..0, while copolymer fractions soluble in toluene form tailing spots or series of spots near the start (R_F = 0–0.30). The fraction soluble in 80% formic acid was investigated similarly. For TLC of this soluble fraction on silica gel, an elution system formic acid–water (2.5 : 1 v/v) was found to separate by the absorption mechanism according to polymer composition and not molecular weight [19]. Such method of separation proceeds only within a very narrow range of formic acid–water ratios. At the above composition, the fractions under investigation exhibit the following R_F values: polycaprolactam 0.80–0.84, block copolymer of character rather close to polyamide 0.71–0.74, polystyrene and block copolymer with character rather close to polystyrene remain at the start. A semiquantitative comparison of the spot intensities on chromatograms on which the same volume amounts of the extract of the individual copolymers were separated showed relatively small amounts or absence of the polycaprolactam fraction. For copolymer C6, which exhibits the relatively most intense spots of polycaprolactam, the homopolyamide content was estimated more exactly by comparison with the spots of a specified amount of polycaprolactam. The fraction soluble in 80% formic acid at room temperature (24 hr extraction, 8.4%) contained less than 30% homopolymer, i.e. $\leq$ 2.5% of the total copolymerization product. In this estimate, it must be noted that the maximum content of homopolyamide is involved in this case. It is very likely that slight hydrolysis of the amide groups occurs during extraction with formic acid, and the splitting of one bond releases a whole chain of the homopolymer from the block copolymer. A similar amount of polycaprolactam was found also in copolymers C3 and C7, while other samples contained less or no polyamide homopolymer.

The occurrence of copolymer fractions differing from the main fraction of the block copolymer in solubility in solvents for the homopolymers can be explained in two ways. They may consist of copolymers of the AB type arising from monofunctional macromolecules of the activator, the character of which will be closer to polystyrene, or of ABA copolymers having a very different ratio of the lengths of the segments A and B, so that the character of one component predominates over the other. The former case may be assumed for the fraction soluble in toluene, because the external blocks A should confer on the copolymer a more pronounced polyamide character irrespective of their length. The latter case represents the fraction soluble in formic acid; it is mainly due to the fact that the polystyrene blocks were prepared by radical polymerization and exhibit a broad $\overline{P}_B$ distribution, also suggested by the viscometric equation discussed above.

These results indicate that suitable choice of reaction conditions and of the type of polymeric activator, and in particular of its reactive terminal groups, allows preparation of block copolymers with well-defined structure. Unlike previous procedures, block copolymers thus prepared contain a minimum amount of the homopolymers.

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REFERENCES

1. D. C. Allport and A. A. Mohajer, in *Block Copolymers* (edited by D. C. Allport and W. H. Janes), pp. 287, 288. Applied Sci. Publ., London (1973).
2. S. W. Shalaby, H. K. Reimschuesel and E. M. Pearce, *Polym. Eng. Sci.* **13**, 88 (1973).
3. M. J. Owen and J. Thompson, *Br. Polym. J.* **4**, 297 (1972).
4. Y. Yamashita, H. Matsui and K. Ito, *J. Polym. Sci., Polym. Chem. Ed.* **10**, 3577 (1972).
5. Y. Yamashita, Y. Murase and K. Ito, *J. Polym. Sci., Polym. Chem. Ed.* **11**, 435 (1973).
6. W. L. Hergenrother and R. J. Ambrose, *J. Polym. Sci.* **A1**, **12**, 2613 (1974).
7. V. V. Korshak, T. M. Frunze, V. V. Kurashev and L. B. Danilevskaya, *Vysokomolek. Soedin.* **A18**, 848 (1976).
8. R. M. Haines and W. A. Waters, *J. chem. Soc.* 4256 (1955).
9. M. R. Kricheldorf, *Makromolek. Chem.* **170**, 89 (1973).
10. J. Stehlíček, J. Šebenda and O. Wichterle, *Colln Czech. chem. Commun.* **29**, 1236 (1964).
11. J. Šebenda and J. Stehlíček, *Colln Czech. chem. Commun.* **28**, 2731 (1963).
12. C. E. H. Bawn, R. Freeman and A. Kamaliddin, *Trans. Faraday Soc.* **47**, 1107 (1950).
13. W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.* **11**, 38 (1953).
14. R. A. Gregg and F. R. Mayo, *J. Am. chem. Soc.* **70**, 2373 (1948).
15. G. V. Schulz, *Z. Elektrochem.* **60**, 199 (1956).
16. R. Waack, A. Rembaum, J. D. Coombes and M. Szwarz, *J. Am. chem. Soc.* **79**, 2027 (1957).
17. P. Outer, C. I. Carr and B. H. Zimm, *J. chem. Phys.* **18**, 830 (1950).
18. C. H. Bamford and M. J. S. Dewar, *Proc. R. Soc.* (*London*) **A192**, 329 (1948).
19. H. Inagaki, F. Kamiyama and T. Yagi, *Macromolecules* **4**, 133 (1971).