Studies on the synthesis of block copolymers containing polyamide-3 as one constituent

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(Received 6 April 1993; revised 4 November 1993)

Block copolymers containing polyamide-3 as one constituent have been synthesized by anionic polymerization. The reaction conditions for the two blocks have to be quite different. Chemical heterogeneity of the products has been studied using thin-layer chromatography. The cyclohexane-insoluble parts of poly(styrene-*b*-acrylamide) and poly(α-methylstyrene-*b*-acrylamide) with high incorporation rate of polyamide as well as the acetonitrile-insoluble part of poly(methyl methacrylate-*b*-acrylamide) are mainly block copolymers. Infra-red measurements confirm these results.

(Keywords: anionic polymerization; block copolymers; polyamide-3)

INTRODUCTION

Anionic polymerization of non-polar monomers is the preferred route to synthesize block copolymers. Consequently, polymers displaying various morphological structures are accessible experimentally. Formation of these morphologies may be regulated by both the molecular weight of each block and the total molecular weight, as well as by the molar ratio of the blocks.

Sequential addition of polar monomers to living anions can be performed successfully, with the exclusion of side reactions, when care is taken to establish defined experimental conditions such as initiator type and concentration, polymerization medium and temperature[1].

This method was used to synthesize block copolymers containing polyamide-3. It is well known that acrylamide undergoes hydrogen-transfer polymerization in the presence of basic initiators. The i.r. spectrum of polyamide-3, synthesized heterogeneously, does not contain polyacrylamide as a by-product[2]. A high value of the ratio of monomer to initiator concentration and a low reaction temperature favour the formation of polyamide-3 with low degree of branching[3]. Macroinitiators, like living polystyrene, poly(α-methylstyrene) and poly(methyl methacrylate) anions, are unknown as initiators for acrylamide to date.

Knowledge of chemical heterogeneity is essential to decide whether the synthesis proceeds without by-products like homopolymers. Thin-layer chromatography (t.l.c.) offers one way to obtain information on this subject. Gankina[4] reported on identification of poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)), poly(styrene-*b*-acrylonitrile) (P(S-*b*-AN)) and poly(methyl methacrylate-*b*-butyl methacrylate) (P(MMA-*b*-BMA)) block copolymers and on the determination of their purity by this method. The results of synthesis and characterization of poly(styrene-*b*-acrylamide) (P(S-*b*-AA)), poly(α-methylstyrene-*b*-acrylamide) (P(αMS-*b*-AA)) and poly(methyl methacrylate-*b*-acrylamide) (P(MMA-*b*-AA)) block copolymers are the subject of this paper‡.

EXPERIMENTAL

Reagents

Purification of acrylamide (AA; Merck, for electrophoresis), LiCl (Merck, P.A.) and *N,N*-dimethylacetamide (DMAc; Merck, P.A.) has been described previously[2]. Tetrahydrofuran (THF; Apolda, P.A.) was refluxed over $LiAlH_4$ and distilled freshly just before use under an atmosphere of dry argon from sodium benzophenone. Styrene was refluxed over calcium hydride and finally condensed into the reation vessel. s-Butyllithium (s-Buli; Aldrich) was used as a 1.4 M solution in cyclohexane/isopentane. The inert gas argon 5.0 (from Messer Griesheim) was purified over 4 A molecular sieve and reduced Ni–Al catalyst.

Polymerization

All operations were carried out under purified argon to exclude oxygen and moisture. Reaction vessels were flame-dried and kept under inert gas. Styrene, methyl methacrylate and α-methylstyrene were polymerized first in THF at −70°C. s-BuLi was used as initiator for styrene, 1,1-diphenylmethylpentyllithium as initiator for methyl methacrylate and tetrameric sodium α-methylstyrene as initiator for α-methylstyrene. After quantitative conversion of the first monomer, the separately prepared position of acrylamide and LiCl in DMAc was added. The polymeriz-

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‡ For specification of the respective block copolymer, the names of the monomers were used despite the fact that acrylamide undergoes hydrogen-transfer polymerization to polyamide-3

0032-3861/94/11/2438–05

ation became heterogeneous owing to reduced solubility of polyamide-3 sequences in DMAc/THF. The product was precipitated into methanol. The polymer was dried in vacuum at 40°C. For further purification, the products were extracted with boiling methanol or 1,4-dioxane or acetonitrile, respectively.

Measurements

Composition of the products was determined by Kjeldahl analysis of nitrogen.

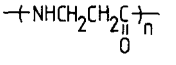
I.r. spectra were recorded on a Specord M80 (Carl Zeiss, Jena); 2.5 mg of the polymer were mixed with 1 g KBr to prepare a tablet.

Kieselgel 60G (Merck) was used as adsorbent for the separation on thin-layer chromatographic plates. The plates were activated at 110°C for 1 h and stored over a saturated aqueous solution of sodium nitrile. In each thin-layer chromatographic experiment the samples ($15\,g\,l^{-1}$) were spotted in a defined order. All developments were performed in two steps with chloroform (eluant for PS and PαMS) or acetone (eluant for PMMA) first and afterwards with trifluoroacetic acid (TFAc) in a normal chamber. After each development, the layers were gently dried. The detection was performed by spraying with Dragendorf reagent[5], acting selectively for nitrogen-containing compounds, and after drying in air with a 3% solution of $KMnO_4$ in concentrated sulfuric acid with subsequent heating at 200°C for 2 h. The stepwise detection of the layers as described is required since the peptide bonds are unstable in acid media.

RESULTS AND DISCUSSION

Synthesis

The block copolymers were synthesized in a mixed solvent. The disadvantage of THF/DMAc lies in its reduced ability to dissolve polyamide-3. Therefore, precipitation occurred for the first time about 1 h after addition of acrylamide solution to living polystyrene, poly(α-methylstyrene) or poly(methyl methacrylate) chains. The synthesized polymers were extracted with boiling methanol or 1,4-dioxane to separate dimers and trimers of polyamide-3. Afterwards, the polymer was extracted with boiling cyclohexane to separate polystyrene. Boiling acetonitrile dissolved poly(methyl methacrylate). The experimental data are given in *Table 1*. The conversion is not quantitative owing to the heterogeneous course of the reaction. The amount of acrylamide converted to polyamide-3:



$$-\!\left[NHCH_2CH_2\underset{\underset{O}{\|}}{C}\right]_n\!-$$

PA3

and incorporated into the block copolymer agrees with that at the beginning of polymerization for P(αMS-*b*-AA). For P(S-*b*-AA) as well as P(MMA-*b*-AA), the incorporation into the polymer is reduced. The results of extraction of the block copolymers are shown in *Table 2*.

Table 1 Conditions of synthesis[a] of block copolymers containing polyamide-3

Sample	$[M_1]^b$ (mol%)	$[M_2]^c$ (mol%)	X^d (%)	$[M_2]^e_{RP}$ (mol%)	Remark
P(S-*b*-AA)					
2	77	23	69	4	AA/DMAc
3	73	27	78	7	AA/DMAc/LiCl
4	71	29	66	10	AA/DMAc/LiCl
P(αMS-*b*-AA)					
1	14	86	48	83	AA undissolved
2	6	94	100	90	AA undissolved
3	29	71	62	75	AA undissolved
4	73	27	59	6	AA/DMAc/LiCl
P(MMA-*b*-AA)					
1	76	24	68	18	AA/DMAc/LiCl
2	73	27	57	6	AA/DMAc/LiCl

[a] Reaction temperature: −60°C for styrene, α-methylstyrene; −78°C for methyl methacrylate; 55°C for acrylamide
[b] M_1 = S, αMS, MMA
[c] M_2 = AA
[d] X = conversion
[e] RP = reaction product

Table 2 Results of extraction of block copolymers containing polyamide-3

	Solvent[a]					
	Methanol		Cyclohexane		Acetonitrile	
Sample	Sol. (wt%)	Insol. (wt%)	Sol. (wt%)	Insol. (wt%)	Sol. (wt%)	Insol. (wt%)
P(S-*b*-AA)						
2	–	–	99.5	0.5	Not	
3	1.6	98.4	93.7	6.3	applic-	
4	7.2	92.8	93.8	7.2	able	
P(αMS-*b*-AA)						
1	3.8	96.2	–	–	Not	
2	–	–	36	64	applicable	
P(MMA-*b*-AA)						
1	–	–	Not		86	14
2	–	–	applicable		77	23

[a] Sol. = soluble, Insol. = insoluble

I.r. spectra

The i.r. spectra of the cyclohexane-insoluble phase of P(S-*b*-AA) as well as of the acetonitrile-insoluble phase of P(MMA-*b*-AA) show the vibrations typical of both blocks (*Figures 1* and *2*). The i.r. data of polyamide-3 are given in ref. 2. In contrast, the spectra of the corresponding soluble phases are those of pure polystyrene for P(S-*b*-AA) and of pure poly(methyl methacrylate) for P(MMA-*b*-AA).

Thin-layer chromatography

Thin-layer chromatographic studies were carried out to decide whether the polymer is free of by-products. Using adsorption thin-layer chromatography the separation of block copolymers and homopolymers was possible[6,7]. The block copolymer and corresponding homopolymers differ in their adsorption behaviour. The difference in polarity of PA3 and PS as well as PA3 and PαMS is greater than that of PA3 and PMMA. Therefore, separation of P(MMA-*b*-AA) from by-products like PMMA and PA3 is more complicated.

*P(S-*b*-AA).* *Figure 3* demonstrates the requirement for extraction of the samples to obtain pure block copolymers. Dimers and trimers of PA3 and PS were separated with methanol and cyclohexane, respectively. The samples, insoluble in cyclohexane, are free of polystyrene in comparison to their raw products and their cyclohexane-soluble phase. In trifluoroacetic acid,

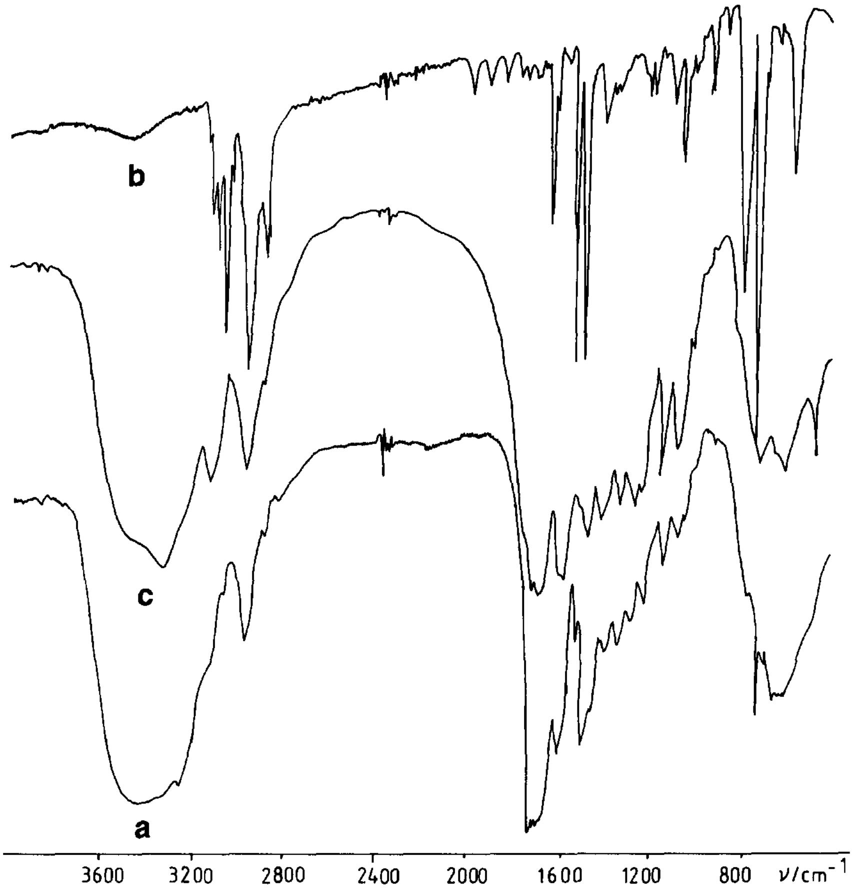


Figure 1 Comparison of i.r. spectra of pure PA3 (c) with cyclohexane-soluble phase of P(S-*b*-AA)4 (b) as well as its insoluble phase in cyclohexane (a)

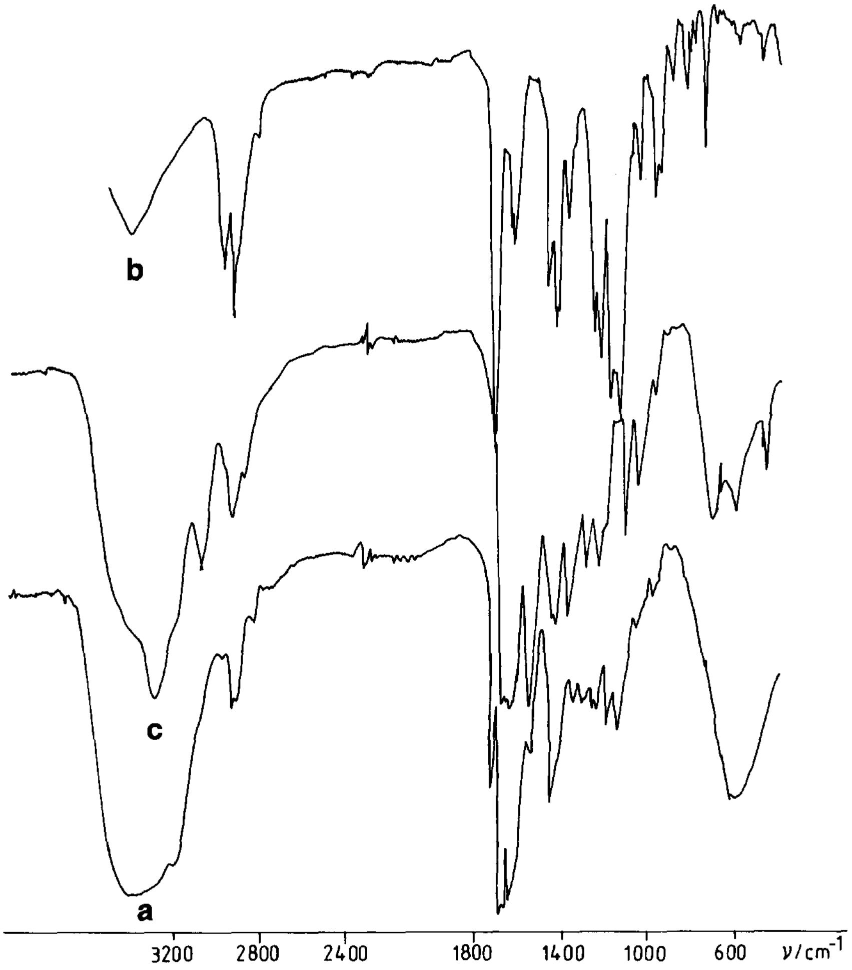


Figure 2 Comparison of i.r. spectra of pure PA3 (c) with acetonitrile-soluble phase of P(MMA-*b*-AA)1 (b) as well as its insoluble phase in acetonitrile (a)

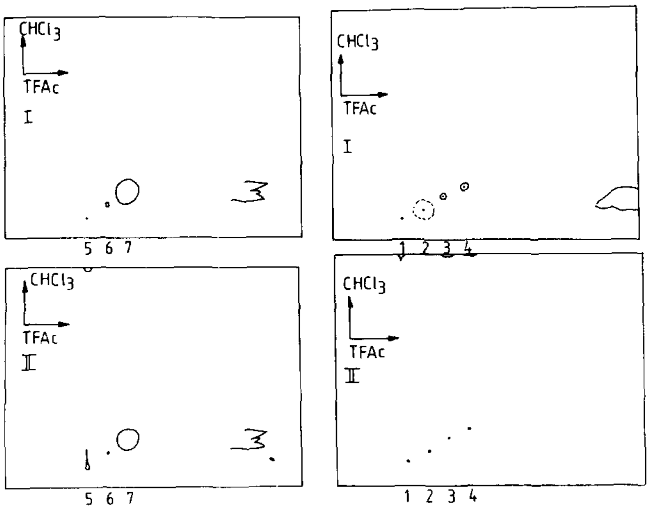


Figure 3 Thin-layer chromatograms of P(S-*b*-AA): 1, polystyrene; 2, polyamide-3; 3, P(S-*b*-AA)3 raw product; 4, P(S-*b*-AA)4 raw product; 5, P(S-*b*-AA)4 soluble in cyclohexane; 6, (P(S-*b*-AA)3 insoluble in methanol, cyclohexane; 7, P(S-*b*-AA)4 insoluble in cyclohexane; (I) detected with Dragendorf reagent; (II) detected with H_2SO_4/$KMnO_4$

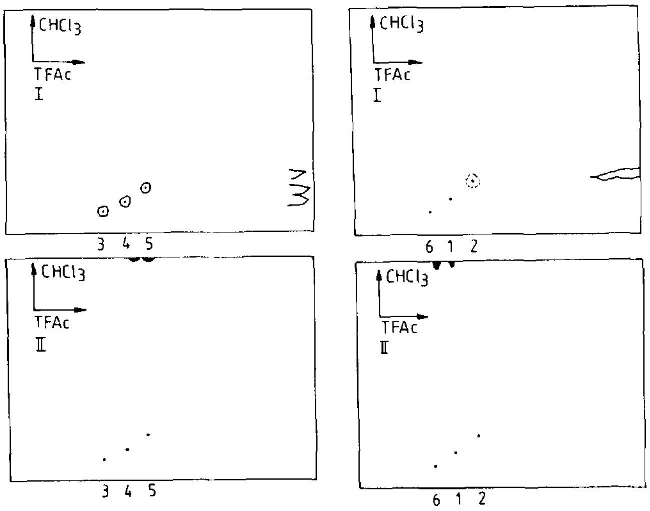


Figure 4 Thin-layer chromatograms of P(αMS-*b*-AA): 1, poly(α-methylstyrene); 2, polyamide-3; 3, P(αMS-*b*-AA)1; 4, P(αMS-*b*-AA)2 raw product; 5, P(αMS-*b*-AA)3 raw product; 6, P(αMS-*b*-AA)4 raw product; (I) detected with Dragendorf reagent; (II) detected with H_2SO_4/$KMnO_4$

a part of the cyclohexane-insoluble phase migrates from the starting point with the front. A polymer zone was detected at the starting point as well as at the front of TFAc with both spraying agents. Obviously, the cyclohexane-insoluble part of the sample consists of two different components—the block copolymer (at the start) and pure or PA3-rich block copolymer (at the front). These results agree with i.r. measurements.

*P(αMS-*b*-AA).* *Figure 4* shows that samples 2 and 3 contain PαMS as well as PA3. In trifluoroacetic acid, samples 1–3 do not differ in their elution behaviour in comparison to pure PA3, whereas sample 4 exhibits only 6 mol%. Taking into account the appearance of polymer spots at the start as well as zones at the front of TFAc (detection I) of samples 1–3, these polymers should consist of two different parts. The polymers are polluted by polyamide-3 and the spots at the start should be caused by poly(α-methylstyrene) linked with polyamide-3. From the second detection with H_2SO_4/$KMnO_4$, the existence of polystyrene is obvious in samples 2 and 3. Taking into account the high incorporation rate of polyamide-3 (*Table 1*) into the product and its low stability in trifluoroacetic acid, the spots of samples 1–3 at the start result from block copolymers. A decision for sample 4 is not possible. Only poly(α-methylstyrene) (detection II) was found.

*P(MMA-*b*-AA).* PMMA migrates with the front in acetone. The raw products of samples 1 and 2 as well as the acetonitrile-soluble phases of them contain poly(methyl methacrylate). In contrast, the insoluble phase remains at the start. This can be detected with Dragendorf reagent as well as with the solution of $KMnO_4$ in concentrated sulfuric acid. This means that the samples consist of methyl methacrylate connected with polyamide-3. Afterwards, the layers were developed in TFAc. A small amount of polyamide-3 is found with Dragendorf reagent, and the starting point is found also with both detecting reagents. This shows that samples extracted with boiling acetonitrile consist of a block copolymer mixed with a small amount of polyamide-3 (*Figure 5*).

CONCLUSION

The good agreement of thin-layer chromatographic data with i.r. measurements confirms the possibility to synthesize the block copolymers P(S-*b*-AA), P(αMS-*b*-AA) and P(MMA-*b*-AA). Obviously, the initiation efficiency of living styrene chains is small. The dramatic change in reaction conditions of the two blocks has to be taken into consideration to evaluate the results. Purification of

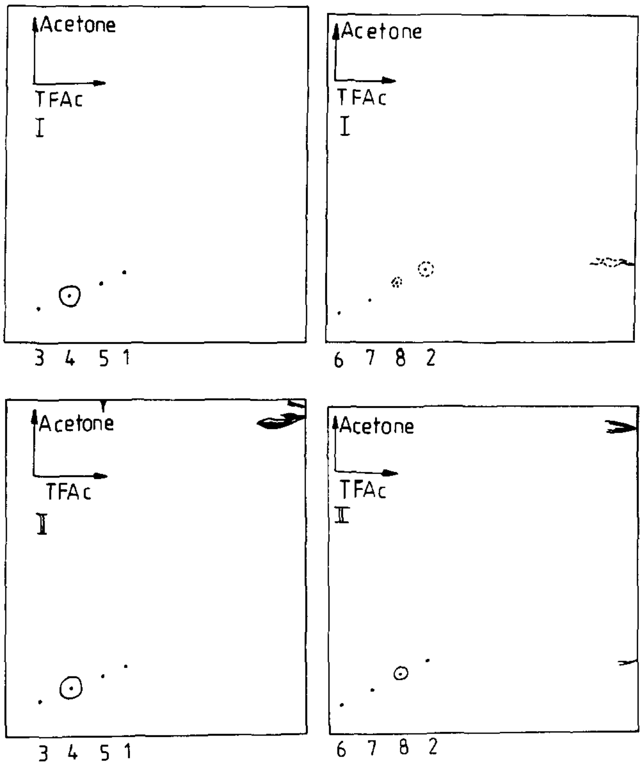


Figure 5 Thin-layer chromatograms of P(MMA-*b*-AA): 1, poly(methyl methacrylate); 2, polyamide-3; 3, P(MMA-*b*-AA)1 raw product; 4, P(MMA-*b*-AA)1 insoluble in acetonitrile; 5, P(MMA-*b*-AA)1 soluble in acetonitrile; 6, P(MMA-*b*-AA)2 raw product; 7, P(MMA-*b*-AA)2 soluble in acetonitrile; 8, P(MMA-*b*-AA)2 insoluble in acetonitrile; (I) detected with Dragendorf reagent; (II) detected with H_2SO_4/$KMnO_4$

the raw products by extraction with boiling acetonitrile for poly(methyl methacrylate), boiling cyclohexane for polystyrene and methanol for dimers and trimers of polyamide-3 is definitely required.

ACKNOWLEDGEMENTS

The authors thank Dr Wedell (Institut für Festkörper- und Strukturforschung e.V.) for discussion of i.r. measurements, Dr Heinemann for discussion of results of t.l.c. and Mrs Görner for carrying out t.l.c. experiments.

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