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CRYSTALLIZATION BEHAVIOUR OF PMMA-b-PEO-b-PMMA TRIBLOCK COPOLYMERS

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ABSTRACT

New synthesized ABA type triblock copolymers of poly /methyl methacrylate/ /PMMA/ and poly /ethylene oxide/ /PEO/ with constant PEO sequence length and varying PMMA sequence length were examined by DSC to study crystalization and melting phenomena. Well defined dependence of melting temperature T_m and crystallinity α of PEO on PMMA sequence size were found in contrast to most of the literature data on other PEO block copolymers. Crystallization of the PEO chains was strongly hampered by the PMMA sequences. From our results we concluded that the crystallization is essentially determined by the chain end's mobility of the crystallizable component.

INTRODUCTION

Crystallization kinetic measurements of triblock copolymers which contain PEO as crystallizable component were undertaken several years ago /1-6/. In most of the cases the PEO chains are the the outer sequences of the triblock, and /or the freezing-in temperature of the non-crystallizable component lies below the crystallization temperature of the PEO. In this event no or only very undefines dependence of the crystallization properties in regard to the block length of non-crystallizable polymer has been found. In this submitted paper we have focussed our interest on well-defined poly /methyl methacrylate/-b-poly /ethylene oxide/-b-poly /methyl methacrylate/ triblock copolymers synthesized by polymerization of methyl methacrylate initiated with living poly /ethylene oxide/ anions /8/. In this case the necessary PEO-dianions are obtained through the polymerization of ethylene oxide with potassium naphthalene in tetrahydrofurane. Products with a narrow molecular weight distribution were obtained. In contrast to many systems investigated in the literature the PEO is inserted between two PMMA sequences. The PMMA glass transition temperature is above the crystallization

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temperature of the PEO. For this reason interesting results could be expected.

EXPERIMENTAL PART

Summary of materials investigated in the present work is given in table 1.

Table 1. Chyracteristics of copolymer samples

Sample code	Structure	$\bar{M}_n$ x10^{-3} /calc./	Mol% PEO	Weight% PEO
ABA IVa	PEO	50	100	100
ABA VIIb	PMMA-PEO-PMMA	1-50-1	98	96
ABA Vb	PMMA-PEO-PMMA	2,5-50-2,5	96	91
ABA Ib	PMMA-PEO-PMMA	5-50-5	92	83
ABA IVb	PMMA-PEO-PMMA	10-50-10	85	71
Blend 1	PEO + PMMA	50 + 10	85	71
Blend 2	PEO-PMMA+PMMA	50-10+10	85	71

The accuracy of the calculated molecular weights was tested by peak analysis of ^{1}H NMR spectra taken on a type HX 90 Bruker spectrometer. Calculated molecular weights are found in well correspondence with spectrometric data. Analysis of the crystallization and melting behaviour was carried out on DSC-20 with the data station 3600. Samples were tempered at 403 K for 10 minutes, cooled with a scanning rate of -8 K/min to 220 K and then heated at a rate of +8 K/min. These measurements were taken under nitrogen atmosphere with dry ice as a cooling agent.

RESULTS AND DISKUSSION

Before systematic investigation of crystallization kinetics could be started we had to make sure of the real existence of linear triblock copolymers because the new way to synthesize such materials was unknown till now in the literature. This was achieved by comparison of DSC heating scans between two samples /ABA IVb and Blend 1/ characterized by the same ratio between PEO and PMMA moles but different in structure. The melting peak observed for the blend of homopolymers completely disappears in the case of the sample ABA IVb. This is an unambigous evidence that in the latter case the sample does not consist of a mixture of the homopolymers. Further evidence obtained from extraction experiments. Branches could be excluded from NMR experiments at 200 MHz. We are sure to have linear triblock copolymers.

The analysis of the crystallization and melting behaviour shows, in contrast to the polymers investigated by Zachmann /4/ as well as by Galin and Mathis /5/, a clear relationship between crystallization kinetics of the PEO and sequence length of the PMMA. The longer the PMMA sequences the more hindered the crystallization of the PEO chains. This hindrance can result in complete disappearance of any crastyllization for the triblock copolymer with the longest PMMA ends /ABA IVb/. Only tempering for 4 months at room temperature yields a small melting peak of ΔH^m = 7,5 J/g at 331,7 K for this sample. Our results are summarized in table 2.

Table 2. Results of DSC Investigations

Sample code	T_m/K	$\Delta H^m/Jg^{-1}$	α^1 / %
ABA IVa	337,3	169,0	83,2
ABA VIIb	332,2	95,8	47,2
ABA Vb	329,5	61,6	30,4
ABA Ib	328,2	51,6	25,4
ABA IVb	-	0,2	0,1
Blend 1	336,2	159,9	78,8
Blend 2	330,0	87,3	43,0

1 Crystallinity was calculated by $\alpha = \Delta H^m/203\ Jg^{-1} \times 100\%$ /7/

Similar results were obtained by the same kind of experimets on a series of triblock copolymers with a central PEO segment having a milecular weight of about 20 000 /9/. We suggest the following explanation /10/. Obviously, the crystallization rate of the PEO segment is mainly determined by the mobility of the chain ends. If the PMMA end blocks are long, then freezing-in occurs on cooling. /Some indications for a microphase separation of the PMMA and PEO blocks at low temperature were obtained from electron microscopy, NMR relaxation times, small angle X-ray scattering, and additional DSC measurements/. Crystallization cannot take place although sufficient space is available for chain folding. Crystallization does occur, however, also for the long PMMA sequences, if at least one PEO end is not chemically fixed on PMMA /Blend 1 and Blend 2/. Electron micriscopy ahows similar microphase structures with about the same length scale for both the blends and sample ABA IVb. /Thanks to Dr. Michler from AdW Halle/.

When the length of the PMMA sequences is shorter, then the PMMA chain can probably not from rigid microphases. The PEO chain ends are not completely fixed, and crystallization occurs, through strongly hampered with raising PMMA sequence length. Further investigations about the crystallization behaviour, the microphase structure, the glass transitions, and about compatibility in such triblock copolymers are planned to ensure our hypothesis.

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