Structure of Styrene and Acrylate Block Copolymers

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ABSTRACT

Using UV light as the energy source and polystyrene- (PS-) or polymethyl methacrylate- (PMMA-) macroinitiators with active aromatic or aliphatic thiyl end groups, PS–PMMA and PMMA–PEA (polyethyl acrylate) block copolymers were synthesized. The molecular weights of both block copolymers increased with increasing reaction time. The reactivity of macroinitiators depended on the type of thiyl groups and monomer and not on the length of the polymer chain. The most reactive were macroinitiators containing resonance stabilized non-substituted or substituted aromatic end groups. The decomposition of the macroinitiators took place over the formation of the thiyl radical and macroradical. The bond length, the bond dissociation energy, and the bond order of macroradical end groups were calculated. The most reactive monomer was ethyl acrylate; the less reactive was styrene. The structure, the molecular weight, and the T_g of the styrene–acrylate block copolymers were determined. The PMMA/PEA block copolymer had two of block's T_gs, the first at 105°C, the second at −24°C, and a third at 16°C which probably represents contacting segments.

INTRODUCTION

Pseudoliving free-radical two-step synthesis of block copolymers leads to the formation of new materials with controlled configuration, molecular weight, and properties. Controlled molecular weight, which is an important structure parameter, can be achieved with free-radical living polymerization using initiators having P–P or S–S groups with low decomposition energies. Such compounds, called iniferters, combine the functions of the initiator, the transfer agent, and the terminator. The macromolecules formed are compounds with active groups on both ends of the polymer chain. When used as macroinitiators, they decompose again and are capable of further mutual reaction or of reactions with other monomers to form block copolymers. The length and configuration of individual blocks determine the character of the block copolymers. Such block copolymers can be formed from compounds with thiyl or any other labile groups on both ends of the macromolecule which, under the influence of UV light, can decompose to a macroradical and a primary radical. The primary radical can initiate a new macroradical or terminate the former one [1–4].

The aim of this work was to study the structure of block copolymers synthesized from polystyrene (PS-macroinitiator), polymethyl methacrylate (PMMA-macroinitiator), and polyethyl acrylate (PEA-macroinitiator). The macroinitiators were prepared with different aliphatic and aromatic disulfide initiators. The structure and mechanism of the reaction were followed by determination of the molecular weights, of the polydispersity, of the molar ratio between the two blocks, of the glass transition temperature, and of the chain end groups. The bond length, the bond energy, and the bond order were calculated.

EXPERIMENTAL

Materials

The following disulfides were used as initiators: Diphenyl disulfide (DPD), bis(2,4,5-trichlorophenyl) disulfide (TCPD), bis(2-aminophenyl) disulfide (2APD), bis(4-aminophenyl) disulfide (4APD), bis(2-nitrophenyl) disulfide (NPD), benzyl methyl disulfide (BMD), dibenzyl disulfide (DBD), dimethyl disulfide (DMD), and tetramethylthiuram disulfide (TMTD). All disulfides were products of Aldrich. The disulfides were purified and dried before use. Styrene (S), methyl methacrylate (MMA), and ethyl acrylate (EA) were products of Rohm and Haas. All monomers were washed with a 10% solution of sodium carbonate and distilled water, dried overnight with nonaqueous sodium sulfate, and twice distilled under reduced pressure. The monomers were used immediately after purification.

Polymerization

Polymerizations were carried out in two steps. In the first step, PS-, PMMA-, and PEA-macroinitiators were synthesized. The monomer without solvent or as a 10 to 50 wt% solution in THF was mixed in a quartz reaction vessel with the selected type and quantity of a disulfide initiator. The reaction temperature was 20 or 35°C. The initiator concentration was between 0.00435 and 0.0367 mol/dm^3 (molar ratio

to monomer 1:100 to 1:1000). The energy source for polymerization was a UV lamp of 254 nm wavelength with an intensity of 4.5 mW/cm^2 at a distance of 2.5 cm. The polymerization time was up to 4 hours. The samples for determination of molecular weight and yield of the reaction were withdrawn from the reaction vessel at different reaction time intervals. After the polymerization was finished, the PS and PMMA were precipitated three times from THF solution to cold methanol (ratio 1:10) and PEA to cold *n*-hexane (ratio 1:10) and dried successively to remove solvents and unreacted initiator. The purity of the polymers was controlled by NMR measurements of the macromolecule end groups and of the unreacted initiator.

In the second step of polymerization, some selected purified macroinitiators were used for the synthesis of block copolymers. The macroinitiator was dissolved in the selected monomer or in an up to 50 wt% solution of monomer in THF in a weight ratio (for a macroinitiator having a certain degree of polydispersity, molar ratios to monomer cannot be successfully determined) of macroinitiator to monomer of 1:100 and than irradiated. The reaction conditions were the same as for the synthesis of macroinitiators. After the polymerization was quenched, the block copolymer was precipitated and dried. Details of preparing the samples are given elsewhere [5].

To evaluate the degree of photopolymerization, control experiments without disulfides under the same reaction conditions as polymerization were carried out as well.

The PS/PMMA block copolymers were separated from homopolymers by using selective Soxhlet extraction and precipitation. PS was first extracted with cyclohexane and then PMMA was extracted with acetonitrile and precipitated from hot ethanol. The last fraction was then successively precipitated with acetonitrile and hot ethanol for PMMA and with cyclohexane for PS homopolymers.
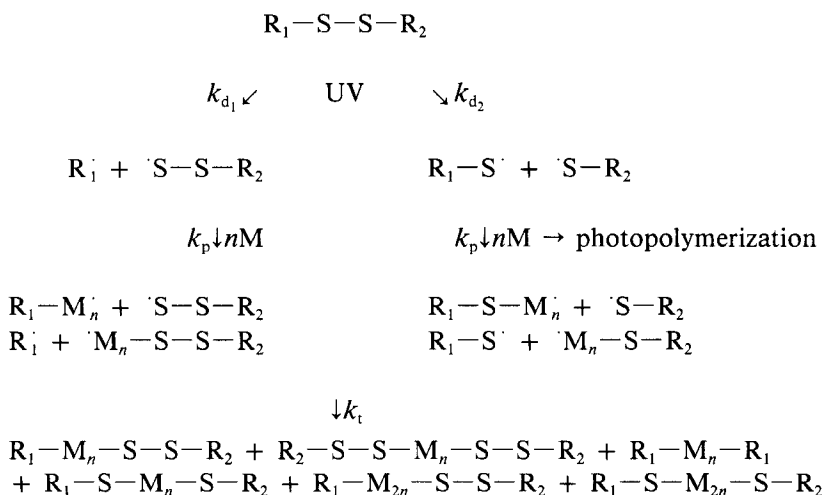
Measurements

The structure and configuration of chain end groups was measured by a Varian VXR 300 MHz NMR spectrometer. All signals were quoted with TMS as an internal standard. The molecular weights were measured by GPC on PL-gel columns with pore sizes of 50, 100, and 1000 nm using THF as the eluent and by viscosity measurements. PS and PMMA standards were used for calibration. A DSC-7 Perkin-Elmer calorimeter was used for the determination of glass transition temperatures.

RESULTS AND DISCUSSION

Using aliphatic or aromatic disulfide initiators having the function of a free-radical living initiator, of a transfer agent, and of a terminator in combination with UV light, two mechanisms of polymerization are possible: The photohomopolymerization of monomers and the decomposition of initiators into two thiyl radicals. These thiyl radicals can further polymerize monomers or terminate the macroradicals. In the second step of the polymerization, UV light decomposes the macroinitiator into a thiyl radical and a macroradical, [5] and both can further polymerize to homo or block copolymers. The homo and block copolymers can be separated by

selective extraction. The degree of photohomopolymerization (reaction without any initiator) depends on types of monomers and initiators and is below 1% in all experiments except for styrene where it is zero. Polymerization takes place even with small amounts of initiator (Fig. 1). The reactivity of the macroinitiators used for the second step of polymerization also depends on the type of monomers and on the type of initiators. The following scheme for the first step of the reaction is possible:

$$R_1 - S - S - R_2$$

$$k_{d_1} \swarrow \qquad UV \qquad \searrow k_{d_2}$$

$$R_1^{\cdot} + {}^{\cdot}S - S - R_2 \qquad\qquad R_1 - S^{\cdot} + {}^{\cdot}S - R_2$$

$$k_p \downarrow nM \qquad\qquad k_p \downarrow nM \rightarrow \text{photopolymerization}$$

$$R_1 - M_n^{\cdot} + {}^{\cdot}S - S - R_2 \qquad\qquad R_1 - S - M_n^{\cdot} + {}^{\cdot}S - R_2$$
$$R_1^{\cdot} + {}^{\cdot}M_n - S - S - R_2 \qquad\qquad R_1 - S^{\cdot} + {}^{\cdot}M_n - S - R_2$$

$$\downarrow k_t$$

$$R_1 - M_n - S - S - R_2 + R_2 - S - S - M_n - S - S - R_2 + R_1 - M_n - R_1$$
$$+ R_1 - S - M_n - S - R_2 + R_1 - M_{2n} - S - S - R_2 + R_1 - S - M_{2n} - S - R_2$$

The First Step of Polymerization

The yield of the formation of the macroinitiators depends on the type of monomers, on temperature, on type, and on concentration of initiators. In Fig. 1 the linear dependence of the yield of the synthesis of the PS-macroinitiator on the concentration of the TCPD is shown. The quantity of initiator consumed decreases with an increase in initial concentration. The consumption is between 0.15 and 0.60
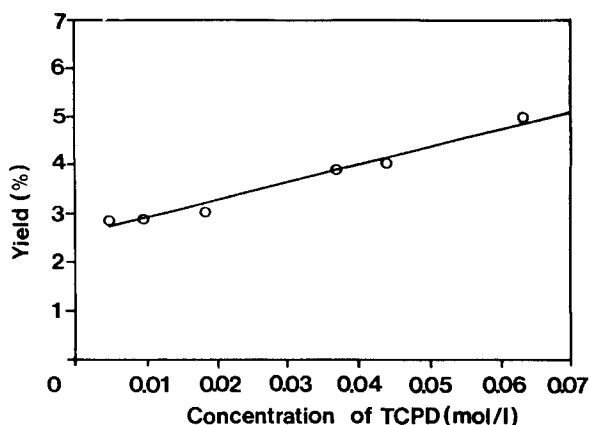

FIG. 1.   The dependence of the polymerization yield of styrene on the initial concentration of TCPD initiator. Reaction time, 4 hours; $T = 20°C$.

parts for the highest and the lowest concentrations of the initiator, respectively. The yield of formation of the macroinitiator [5] and its molecular weight increases (Fig. 2) with the reaction time and conversions for all monomers and for all macroinitiators. The increase of molecular weight with conversion is not linear at the beginning of polymerization, but with increased conversion the molecular weights for all monomers increase linearly. According to the criteria for living polymerization [6], the nonlinear dependence of the molecular weight on conversion is an indication of pseudoliving polymerization.

Second Step of Polymerization

All unreacted initiator was removed from the macroinitiators formed before they were used for the second step of polymerization. Three types of reactions are possible: photohomopolymerization, polymerization initiated by primary radicals, and block copolymerization of macroradicals. To determine the formation of homopolymer, the copolymers were successively extracted with cyclohexane for PS and with acetonitrile and hot ethanol for PMMA. The portion of the block copolymer in the product was between 92.1 and 96.6% [5] and increased linearly with reaction time (Fig. 3). The rest was only unreacted PS-macroinitiator. In the second
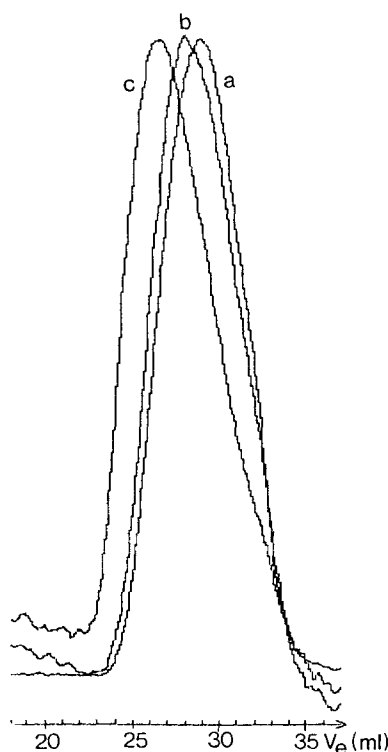

FIG. 2.   GPC chromatograms of the PEA/DPD macroinitiator (molar ratio 1000:1). $T = 20°C$, 10% EA concentration in THF. Hours of reaction time: (a) 14, (b) 18.8, (c) 22.
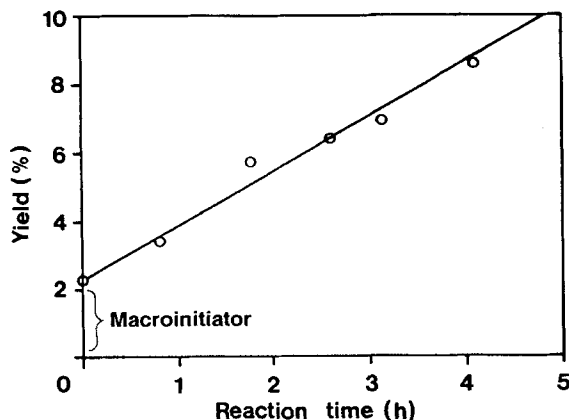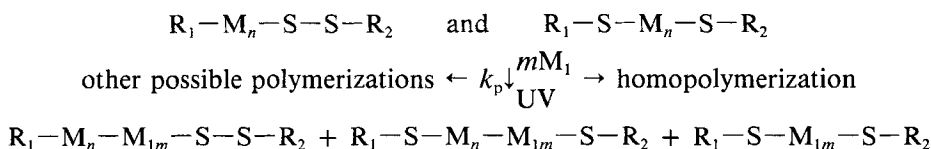
FIG. 3.   The dependence of the yield (portion of polymer in the reaction mixture) of MMA with PS/TCPD macroinitiator on the reaction time. T = 20°C.

step of polymerization, no homo-PMMA was detected. The following scheme is possible for block copolymerization.

$$R_1-M_n-S-S-R_2 \quad \text{and} \quad R_1-S-M_n-S-R_2$$

$$\text{other possible polymerizations} \leftarrow k_p \downarrow \begin{matrix} mM_1 \\ UV \end{matrix} \rightarrow \text{homopolymerization}$$

$$R_1-M_n-M_{1m}-S-S-R_2 \ + \ R_1-S-M_n-M_{1m}-S-R_2 \ + \ R_1-S-M_{1m}-S-R_2$$

There are two possibilities for the decomposition of the macroinitiator end groups from the macromolecule. The first is the decomposition of the Polymer-SC bond (a), and the second is the decomposition of the Polymer-S-C bond (b).

$$\text{Polymer}-S-R \rightarrow \text{Polymer}\cdot \ + \ \cdot S-R \qquad (a)$$
$$\searrow$$
$$\text{Polymer}-S\cdot \ + \ \cdot R \qquad (b)$$
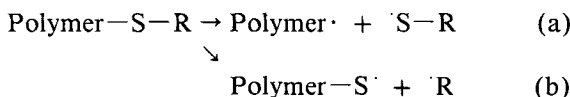
The bond length, the bond energy, and the Mulliken bond order values were calculated with the SPARTAN electronic structure program [7]. The semiempirical AM1 method [8] was used. The bond lengths, bond energies, and Mulliken bond order values are for longer bonds with lower bond energy and lower bond order values in all cases of Polymer-SC bonds. Due to the semiempirical method used, the values are useful only as comparative values. We can predict that the higher bond length and lower bond energy favor the decomposition of the Polymer-SC Bond and the formation of Polymer·Macroradical and Primary Thiyl Radical. This is in agreement with the observed and calculated ^{13}C-NMR chemical shifts of signals of atoms where PS–PMMA blocks are bonded together. The shifts correspond to the C—C bond, not to the C—S bond. There are only small differences between the bond length, bond energy, and bond order values of the thiyl radical on the head and on the tail of the monomer units. From this we can predict that macroradical growth is spontaneous on both sides in the second step of polymerization. The cleavage of the macroinitiator end groups and the insertion of new monomer into

the chain are proportional to the UV absorption energy. This leads to an increase of the molecular weight in the second step of polymerization (Table 1).

The reactivity of a macroinitiator depends on the type of reactive end group and on the type of monomer (Table 1). MMA reacts more easily than styrene both with PS- and with PMMA-macroinitiator. Due to their high molecular weight and therefore poorer solubility in monomer and also low concentration of reactive end groups, PEA-macroinitiators are hardly capable of further polymerization. The type of end groups has an important influence on the yield of the reaction and on molecular weights in the formation of macroinitiators and in the formation of block copolymers. The resonance stabilized end groups of TCPD thiyl radical have the highest reactivity. The aliphatic disulfides, such as DMD, give no resonance stabilized radicals. The reactivity of macroradicals having methyl thiyl end groups is low in the first [5] and the second step (Table 1), which leads to lower yields and lower molecular weights. The polydispersity of all three investigated macroinitiators was around 2. The polydispersity of block copolymers increased up to 3.

The polymer chain length of a macroinitiator does not influence the reactivity of the macroradical since reactivity depends only on the reactivity of the thiyl end groups. For example, the molecular weight of the PS-macroradical with 4APD end groups increased from 8,600 to 45,500 g/mol after polymerization with MMA. This molecular weight is close to the molecular weight of PMMA homopolymer after the first step of polymerization (36,600 g/mol) plus the molecular weight of PS-macroinitiator (8600 g/mol):

PS-macroradical + MMA → PS–PMMA block copolymer, M_n = 45,500 g/mol

PS-macroinitiator + PMMA–homopolymer, $M_{nPS} + M_{nPMMA}$ = 45,200 g/mol
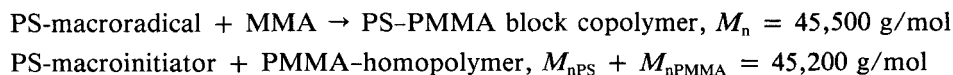
The same PS-macroradical increases the molecular weight after the second step of polymerization with styrene from 8,600 to 14,000 g/mol. This is understandable since the reactivity depends only on the decomposition of the end groups due to the different bond energy, on the bond length of the C—S group, and on the type of monomer used for the second step of polymerization. Similar results are obtained also by NMR measurements of the end groups of PMMA homopolymer and PS–PMMA block copolymer. It can be seen in Fig. 4 that the ^{13}C-NMR signals of the 4APD end groups are similar for PMMA homopolymer and for PS–PMMA block copolymer but different for PS-macroinitiator. Also, the spectra of the homopolymer PMMA and the PMMA block in PS–PMMA block copolymer are similar. Thus it is confirmed that the second block is formed by a similar mechanism and has a similar reactivity, structure, and conformation compared to the homopolymer.

Another possible method of block copolymer characterization is the glass transition temperature (T_g), provided that the two homopolymers have different T_g values. This is not the case for PS/PMMA block copolymers since both homopolymers have their T_g near 105°C. Two values of T_g were found for the PMMA/PEA block copolymers (Fig. 5). The first, at −24°C, corresponds to PEA blocks, and the second, at 105°C, corresponds to PMMA blocks. There is also a small signal at about 16°C which may belong to segments where two blocks are bonded together. Since the concentration of these segments is some hundreds of times smaller than the concentration of each monomer in the chain, the value of the third T_g of the block copolymer cannot be more precisely determined.

TABLE 1. Comparison of Different Measured and Calculated Parameters for the Second Step in the Polymerization of Styrene, Methyl Methacrylate, and Ethyl Acrylate Using PS- and PMMA-macroinitiators. Reaction time: 4 hours

Macroinitiator	Temperature, C	Monomer	Molar ratio I/II block[a]	Weight gain[b]	M_n (g/mol) of the macroinitiator	M_n (g/mol) of the copolymer
PS–2APD	35	S	—	1.6	11,300	14,900
PS–TCPD	35	S	—	1.3	12,000	16,000
PS–DPD	35	S	—	1.1	6,400	8,900
PS–DBD	35	S	—	1.0	7,100	12,200
PS–TMTD	20	MMA	1:8.3	6.0	8,300	48,900
PS–TCPD	20	MMA	1:6.6	5.6	5,200	32,900
PS–DPD	20	MMA	1:7.4	8.2	7,300	46,000
PS–4APD	20	MMA	1:4.9	4.5	8,600	45,500
PS–NPD	20	MMA	1:7.4	7.3	8,400	54,400
PS–DMD	20	MMA	1:3.4	3.3	11,000	41,900
PMMA–DPD	20	MMA	—	4.0	54,300	133,200
PMMA–2APD	20	MMA	—	4.7	31,000	83,900
PMMA–DBD	20	MMA	—	5.9	13,400	45,100
PMMA–TCPD	20	EA	1:0.49	5.2	43,700	73,900
PMMA–BMD	20	EA	1:0.45	2.6	32,900	38,000
PMMA–DPD	20	EA	1:0.19	1.7	21,800	26,300
PMMA–DPD/THF	20	EA	1:3.16	4.2	27,300	97,500

[a]Calculated from ^{1}H-NMR measurements.
[b]Weight gain means the factor increase of product weight in the second step (starting point from 1) but includes the loss of weight during three precipitations.
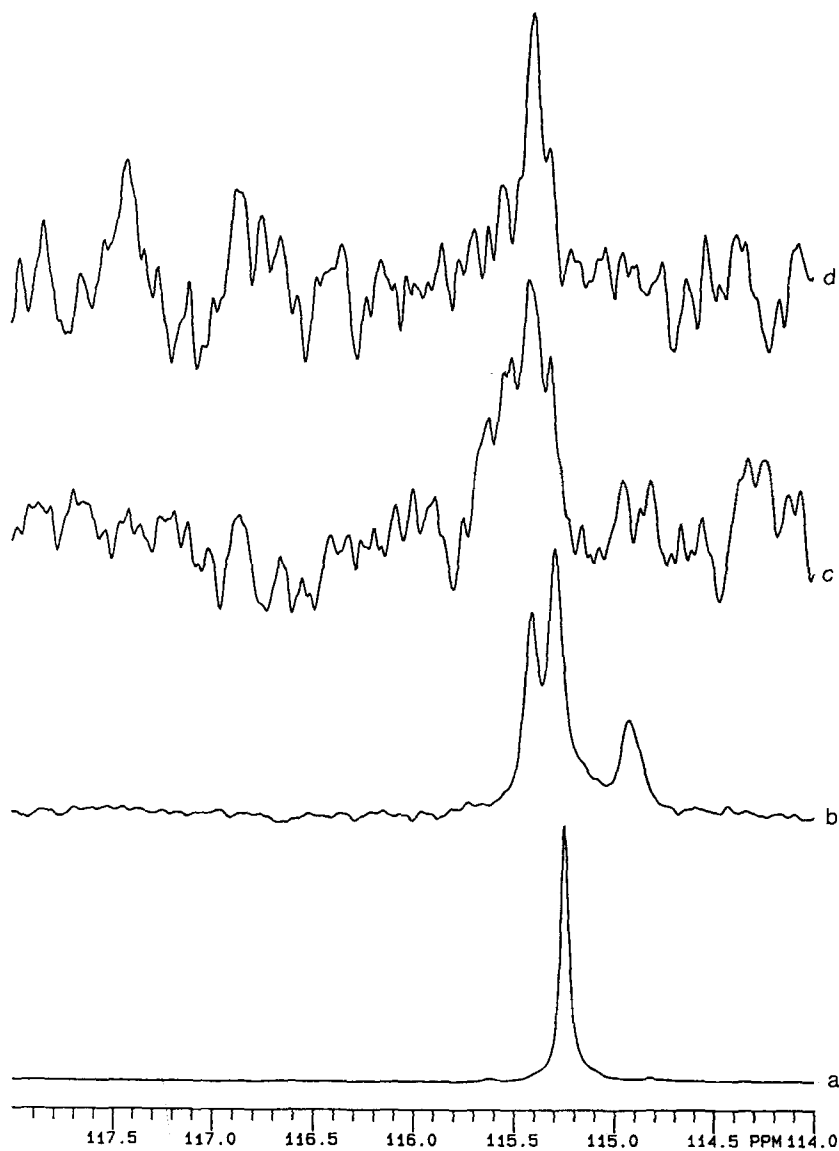
FIG. 4.   The aromatic region of the ^{13}C-NMR spectra of the C_3 atoms of the 4APD end groups. (a) 4APD before reaction, (b) in PS-macroinitiator, (c) in PS/PMMA, and (d) in PMMA/PMMA block copolymers.
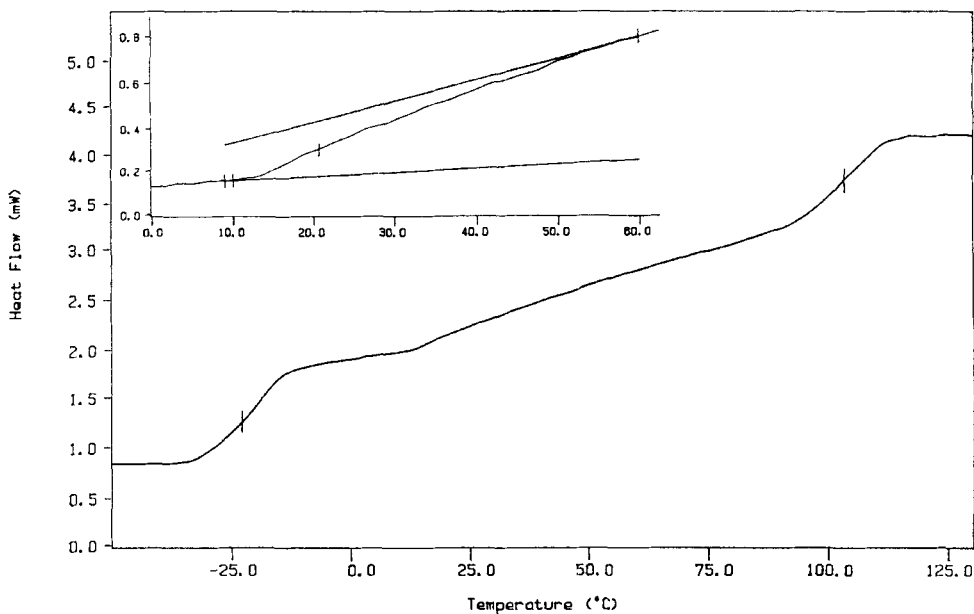
FIG. 5.   The DSC curve of the block copolymer PMMA/PEA.

CONCLUSION

By using disulfide initiators, pseudoliving polymerization and block copoly-
merization of styrene and acrylates takes place. The molecular weight increases with
the reaction time in the first and second steps of polymerization. The reactivity of
the macroradicals depends on the type of end groups. Aromatic resonance stabilized
end groups are more reactive than aliphatic unstabilized ones. If a block copolymer
is formed of two polymers having different T_g values, the block copolymer exhibits
the two T_gs of the blocks plus a small T_g between them which probably belongs to
segments where the two blocks are bonded together.

ACKNOWLEDGMENT

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