Modification of Unsaturated Polyesters by Poly(ethylene glycol) End Groups

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ABSTRACT: This article reports on the modification of unsaturated polyesters by poly(ethylene glycol) end groups in order to influence the solution behavior in styrene and to modify mechanical properties of the cured resin. The synthesis was done by the reaction of a carboxyl-terminated unsaturated polyester with various poly(ethylene glycol) mono-methyl ethers of molecular weights from 350 to 2000 g/mol. The characterization and curing properties of the synthesized block copolymers are presented. The glass transition temperatures decrease with increasing length of the poly(ethylene glycol) end groups. The introduction of long poly(ethylene glycol) end groups (2000 g/mol) leads to a phase separated and partly crystalline block copolymer with a melting point of 48°C. The block copolymers can be easily diluted in styrene to create the curable resins. The mixtures containing the block copolymers with the short poly(ethylene glycol) end groups (350 and 550 g/mol) could be cured in a reasonably short time. Compared to commercial unsaturated polyesters the mechanical testing revealed that the tensile strength is decreasing while the elongation is increasing. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 527–537, 1997

Key words: unsaturated polyester; poly(ethylene glycol); block copolymer; toughness; crosslinking

INTRODUCTION

Unsaturated polyesters are one of the most important matrix resins for composite applications. They possess a wide range of properties and are used in marine, automobile, construction, sport, and furniture applications. In these applications reinforcing glass fibers are embedded in the unsaturated polyester matrix. Also, other components such as fillers, additives, and pigments may be present.[1]

In the development of high-performance polymer composites much attention has been paid to the improvement of fracture toughness and impact resistance. This can be done by chemical or physical methods. One possibility is the addition of dispersed elastomer particles such as butadiene-acrylonitrile rubbers into the unsaturated polyester matrix.[2] These low profile additives form a heterogeneous blend with the unsaturated polyester. Chemical modification can be done either by incorporation of long-chain diols (e.g., diethylene glycol, dipropylene glycol, triethylene glycol) or by incorporation of long-chain saturated acids (e.g., adipic acid) into the polyester chain during the polycondensation reaction.[3] A disadvantage of this method is the fact that a large amount of these compounds must be used in order

to impart a sufficient effect on toughness, which in turn, results in sacrifice of other properties. Another possibility for chemical modification is copolymerization of liquid hydroxyl or carboxyl terminated rubbers or poly(ethylene glycol)s. The synthesis of unsaturated polyesters containing poly(ethylene glycol) segments in the polymer main chain has been reported recently. Tong et al.[4–7] have studied the mechanical properties of unsaturated polyesters containing poly(ethylene glycol)s with number-average molecular weights ranging from 600 to 10000 g/mol. Tensile and flexural properties decrease with increasing molecular weight of the poly(ethylene glycol) segment while the impact strength, elongation, and water absorption have an inverse effect. Pandit et al.[8] have studied the effect of unsaturated poly(ethylene glycol) impact modifiers on the mechanical properties of unsaturated polyesters. Poly(ethylene glycol) segments have also been used to reduce the glass transition temperature of crosslinked lignin based polyesters[9] and in flame-retardant unsaturated polyesters used for rocket propellants.[10–12] Poly(ethylene glycol) segments can also be used to get water-soluble resins of unsaturated polyesters for coating applications.[13]

In this article we are presenting the modification of unsaturated polyesters by poly(ethylene glycol) end groups in order to influence the solution behavior and the mechanical properties of the cured resin. The synthesis is done by a coupling reaction of a carboxyl-terminated unsaturated polyester with poly(ethylene glycol) mono-methyl ethers of various molecular weights. This results in block copolymers, which are predominately of AB type. The conversion of the typical polar end groups to poly(ethylene glycol) end groups should improve the flexibility of the polymer chain and also improve the flexibility of the cured material. The intermolecular chain interactions will also change considerably. Instead of hydrogen bonds, which are responsible for aggregation and the high viscosity in styrene, van der Waals interactions are dominant. The reduction of polar chain interactions could lead to lower viscosity, which is an advantage during processing the resin.

EXPERIMENTAL

Materials

1,2-Propane diol (Merck, 99%), phthalic anhydride (Merck, 98%), and maleic anhydride (Merck, 99%) were used without further purification. Poly(ethylene glycol) mono-methyl ethers with a number-average molecular weight ranging from 350 g/mol to 2000 g/mol (Aldrich) were dried under vacuum at 120°C for 3 h before use. Toluene and styrene were of standard laboratory grade and were used as received. A redox type initiator system (methyl ethyl ketone peroxide Butanox M50 and cobalt octoate NL-49P) from Akzo Nobel was used for the curing reactions.

Characterization

Infrared (IR) spectra were measured in KBr with a Bio-Rad Digilab FTS-40. Nuclear magnetic resonance (NMR) spectroscopy measurements were done on a Bruker AC 250 (^{1}H) and on a JEOL GSX 270 (^{13}C) in CDCl$_3$. Molecular weight determination was done by end group titration corresponding to the ASTM D 1045–80 standard. These results were compared to gel permeation chromatography (GPC) measurements in THF with a Waters HPLC-System equipped with two PL-columns (1000 Å and 500 Å pore sizes) and an UV (254 nm) and a RI detector. Polystyrene standards were used for the calibration with 1,2-dichloro-benzene (Aldrich) as internal standard. Thermal gravimetric analysis and differential scanning calorimetry were carried out with a Netzsch STA 409 and Mettler DSC 30 systems. The heating and cooling rates were 10 K/min and the analysis was done under nitrogen. The curing reaction of the resins containing the block copolymers and styrene was observed at 25°C with a thermal scanning rheometer from Polymer Laboratories. Mechanical testing of cured block copolymer castings was done with an Instron 1175 tensile strength testing machine equipped with a 5 kN load cell. The draw ratio was 2.0 mm/min and specimens of dumbbell shape (size: 100 × 10 × 4 mm) were used.

Polymer Synthesis

Synthesis of Unsaturated Polyester 1

In a polycondensation reactor, equipped with a mechanical stirrer, an argon inlet and a water condenser 47.94 g (0.63 mol) 1,2-propane diol, 59.25 g (0.40 mol) phthalic anhydride, 19.61 g (0.20 mol) maleic anhydride and 6.7 g (5.0 wt %) toluene were added. The mixture was stirred under continuous argon flow for 9 h and the temperature was increased from 160°C at the begin-

Table I Composition of Synthesized Polymers 1–6

Sample	MA/PA Ratio	M_n of PEG Segment (g/mol)
1	1 : 2	—
2	1 : 2	350
3	1 : 2	550
4	1 : 2	750
5	1 : 2	2000
6	2 : 1	350

ning of the reaction to 230°C at the end of reaction. Samples for end group titration were collected every hour for monitoring the progress of the reaction.

Synthesis of Unsaturated Block Copolymers 2–6

For the synthesis of the block copolymers poly(ethylene glycol) mono-methyl ethers with different molecular weights (350–2000 g/mol) were used. The ratio of maleic anhydride to phthalic anhydride (MA/PA) was 1 : 2 (samples **2–5**) and 2 : 1 (sample **6**), respectively. The compositions

of the different block copolymers are summarized in Table I.

The reaction was carried out according to a two-step process (Fig 1). The first step is equivalent to the synthesis of conventional unsaturated polyesters. After the end of this step the acid number was determined by titration with 0.1 N KOH and the calculated equivalent amount of the poly(ethylene glycol) mono-methyl ether was added. The coupling reaction was continued for 5 h at 230°C under an argon flow. The completion of the end group coupling reaction was monitored by GPC measurements from samples collected hourly from the reactor. The block copolymers, which were collected prior to the addition of styrene, were characterized and are listed in Table I as samples **2–6**.

All investigations of the polyester and of the block copolymers were done without further purification of the samples.

Dilution of Unsaturated Block Copolymers in Styrene

The synthesized polyester **1** and the block copolymers **2–5** were diluted to a styrene content of 30

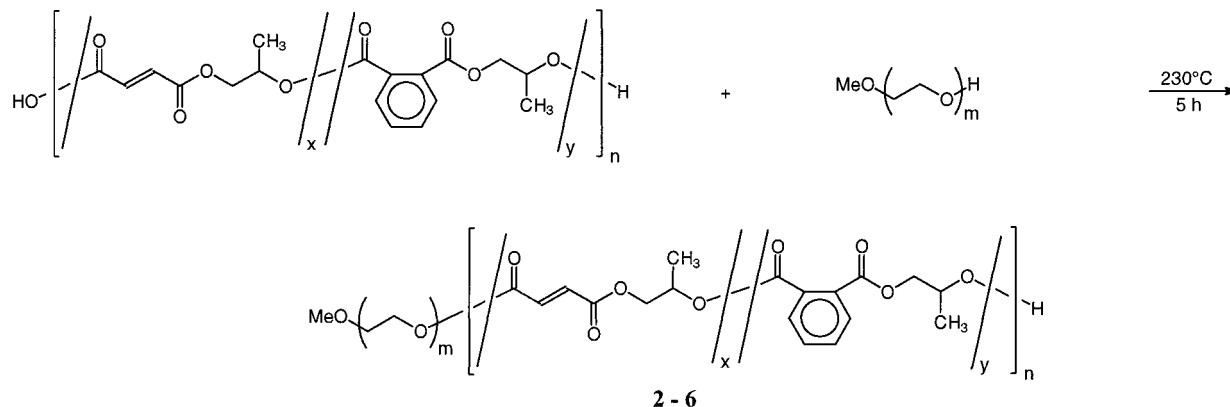**First Step:**
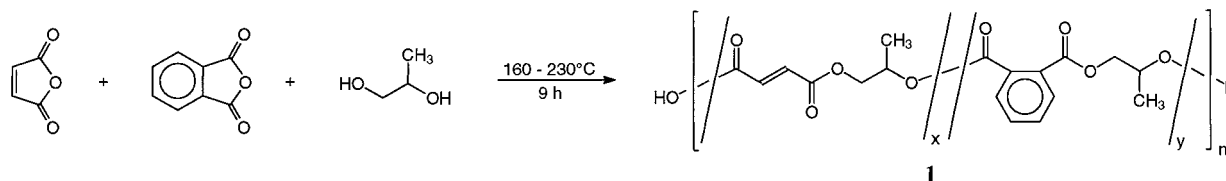
Second Step:

Figure 1 Two-step synthesis of unsaturated polyesters with poly(ethylene glycol) end groups.

Table II   Composition of Investigated Resins I–VII

Resin	Polymer	Styrene Content (wt %)
I	1	30
II	2	30
III	3	30
IV	4	30
V	5	30
VI	6	20
VII	6	40

wt % to give the resins **I–V** (Table II). Block copolymer **6** was diluted to 20 and 40 wt % styrene (resins **VI** and **VII**). The dilution was done immediately after the completion of the block copolymer synthesis, which is important in order to achieve a homogeneous solution in styrene. The reaction melt was allowed to cool to 180°C and then added to the styrene under vigorous stirring. The styrene was also cooled with ice to avoid the temperature to exceed 70°C preventing thermally initiated crosslinking.

The resins of the block copolymers are stable fluids and have lower viscosities than those of the unsaturated polyester so that they can be easily casted at room temperature.

RESULTS AND DISCUSSION

Synthesis and Characterization of Unsaturated Polyester 1

For an end group modification reaction is done with a hydroxy-terminated compound it is in prin-

ciple necessary to use an excess of the dicarboxylic acid component in order to increase the acid functions at the chain ends. This is, however, difficult because of the easy sublimation of phthalic anhydride from the reaction mixture. Instead, we used a small excess of 1,2-propane diol, which gives a polyester with hydroxyl as well as carboxyl end groups. By titration it is possible to determine the number of carboxyl groups in the reaction mixture. For this purpose we made the assumption that every polyester chain has on average one acid end group.

The via titration determined number-average molecular weight (M_n), and the number-average molecular weight determined by GPC is shown in Table III. The values are in good agreement. The M_n was also determined during the polycondensation reaction, and it can be seen that the desired M_n is achieved after a 9-h reaction time (Fig. 2). The structure of the polyester was verified by ^{1}H-NMR. The composition of the polyester corresponds to the initial ratio of maleic anhydride (MA) to phthalic anhydride (PA) indicating that no phthalic anhydride was lost by sublimation. A complete change in the conformation of the maleic anhydride segment from *cis* to *trans*, after incorporation in the polyester, was also confirmed. This is in agreement with the literature.[3]

Synthesis of Unsaturated Block Copolymers 2–6

There are two general ways to synthesize block copolymers with polyester segments. One way is to add the monofunctional component A directly to the melt condensation reaction mixture. This is a one-step synthesis of the block copolymer and

Table III   Characterization of Synthesized Polyester Segments and the Corresponding Block Copolymers

Sample	Acid Number[a]	Polyester Segment $M_n{}^{b}$ (g/mol)	$M_n{}^{c}$ (g/mol)	M_w/M_n	Block Copolymer $M_n{}^{c}$ (g/mol)	M_w/M_n
1	35.1	1600	1470	2.0	—	—
2	34.1	1650	1390	1.7	1330	1.7
3	39.2	1430	1150	1.5	1190	1.6
4	35.1	1600	1450	2.0	1430	2.0
5	37.5	1500	1310	1.8	1380	2.8
6	45.4	1240	1290	1.7	1080	1.5

[a] Titration with 0.1 N KOH and expressed as mg KOH/g sample.
[b] Determined by end group titration.
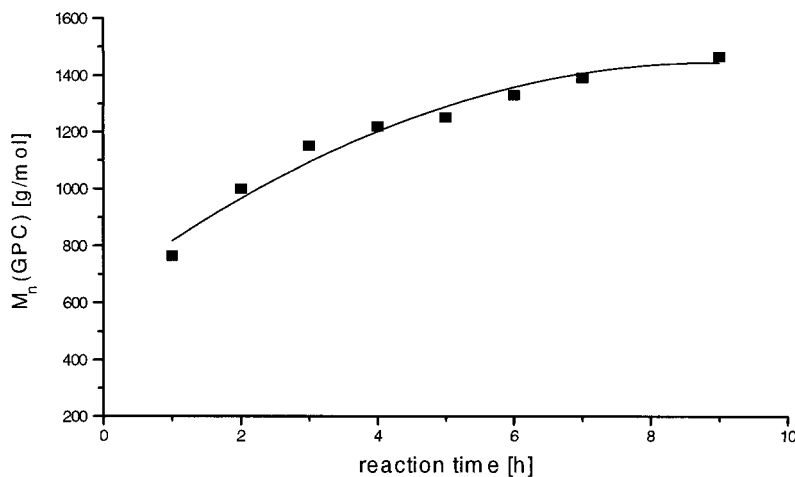[c] Determined by GPC in THF with RI detection.

Figure 2 Progress of the polycondensation reaction of the unsaturated polyester **1**. M_n was determined by GPC in THF (RI detection).

the molecular weight will be adjusted by the amount of monofunctional component A.[14]

A disadvantage of this method is the difficulty to control the molecular weight distribution of the unsaturated polyester segment. The high molecular weight monofunctional reagents that are necessary for a block copolymer are less reactive compared to similar low molecular weight monofunctional reagents typically used in unsaturated polyesters for molecular weight control. A one-step synthesis can more likely result in a mixture of the desired block copolymer, unreacted monofunctional reagent A, and unsaturated polyester B.

Because of this disadvantage we selected a two-step route to synthesize unsaturated block copolymers (Fig. 1). The first step is the well-known polycondensation reaction of the monomers phthalic anhydride, maleic anhydride, and 1,2-propane diol, which leads to a polyester with hydroxyl and carboxyl end groups. The second step consists of the addition of the poly(ethylene glycol) mono-methyl ether and its coupling reaction with the carboxyl end groups leading to a block copolymer. The two separate steps offer several advantages compared to the one-step method. The polydispersity of the polyester segment will become lower and it is possible to control its length by varying the reactant composition in the first step. No excess of poly(ethylene glycol) mono-methyl ether is necessary, as it is possible to determine the number of acid end groups by titration. The coupling reaction can be effectively completed by continuing the reaction during the second step. This synthesis route leads mainly to AB diblock copolymers. There will, of course, also

be a fraction of ABA triblock copolymers and of unreacted unsaturated polyester B. Nevertheless, the obvious advantages convinced us to use the two-step process to synthesize block copolymers with an unsaturated polyester segment and a flexible poly(ethylene glycol) segment.

The progress of the two-step reaction is shown for block copolymer **4** in Figure 3. The number-average molecular weight (M_n) decreases after adding the poly(ethylene glycol) mono-methyl ether, which is due to the addition of a lower molecular weight component to the polyester melt and due to transesterification reactions. The reaction is completed after 3 h and the molecular weight becomes nearly constant. This behavior of the polycondensation reaction is similar for all investigated samples. Table III summarizes M_n of the unsaturated polyesters after the first step of reaction and of the corresponding block copolymers **2–6** (determined by titration of the acid groups and by GPC analysis). An expected shift to higher molecular weights for the block copolymers was not observed. In some cases the molecular weights are slightly lower than those of the corresponding polyester segments. This may indicate that the hydrodynamic volume of the block copolymers does not increase with the addition of the poly(ethylene glycol) segment.

The effectiveness of the coupling reaction could be confirmed by a combination of GPC, IR, ¹H-NMR, and ¹³C-NMR methods. The absence of a shoulder in the GPC diagram of the block copolymers at the position of the neat poly(ethylene glycol) mono-methyl ether revealed that there is no substantial amount of unreacted poly(ethylene
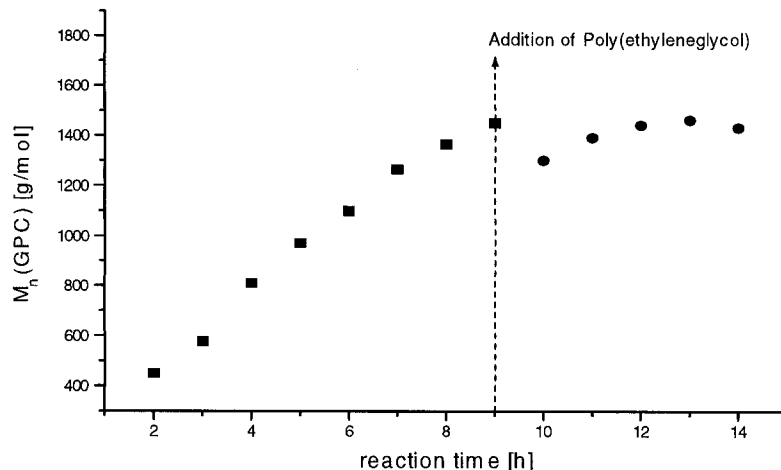
Figure 3   Progress of the polycondensation reaction of the block copolymer **4**. M_n was determined by GPC in THF (RI detection).

glycol) mono-methyl ether present (Fig 4). The IR spectrum of block copolymer **3** in Figure 5 shows no broad signal at wave numbers typical for acid groups ($3500–3000$ cm^{-1}), which is present in the IR spectrum of the polyester from the first reaction step. The differences between the ^{13}C-NMR spectra of the pure poly(ethylene glycol) mono-methyl ether [Fig. 6(a)] and of the block copolymer **4** [Fig. 6(b)] also give a good information about the coupling. The carbons of the methyl ether (**d**) and of the adjacent methylene group (**c**) have the same chemical shifts in both spectra (58.6 ppm and 71.5 ppm). The chemical shifts (61.2 ppm and 72.2 ppm) of the carbons of the two methylene groups (**a** and **b**) next to the hydroxyl

group of the poly(ethylene glycol) mono-methyl ether are shifted to the region of the carbons of the polyester block (64–69 ppm) if connected by an ester linkage to the polyester segment (**a*** and **b***). The weak intensity of the signals at 61.2 ppm and 72.2 ppm in the spectrum of the block copolymer indicates that only a relative small amount of unreacted poly(ethylene glycol) mono-methyl ether is present, but the major part of it has reacted with the carboxyl end groups of the polyester block. The composition of the block copolymers can be determined with the ^{1}H-NMR spectroscopy. The calculated (one poly(ethylene glycol) segment per polyester segment) and the determined values are in good agreement (see Ta-
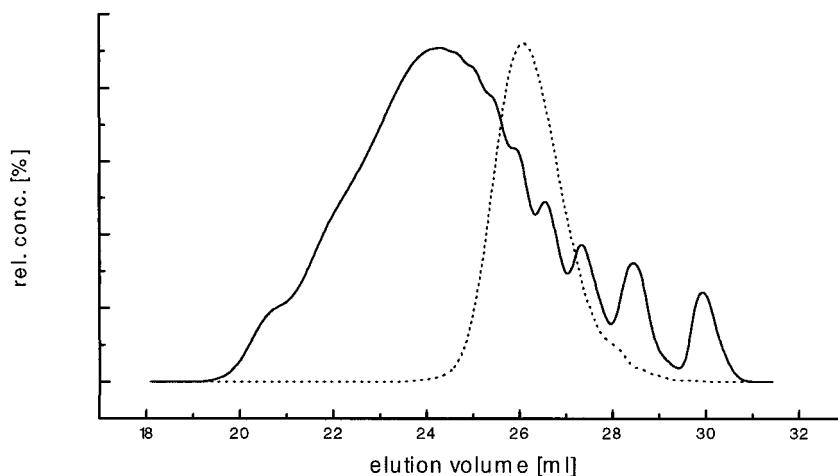

Figure 4   GPC diagrams of the block copolymer **4** (solid line) and of the pure poly(ethylene glycol) mono-methyl ether (dotted line). These diagrams were measured by using the RI detector.
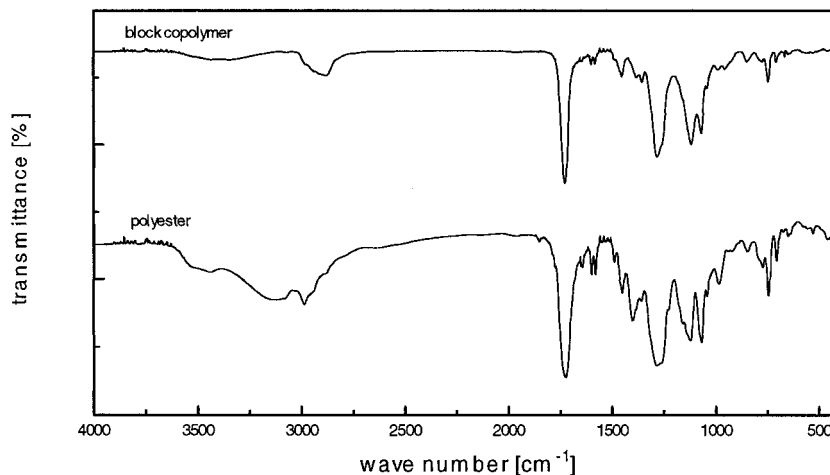
Figure 5 Infrared spectra of block copolymer **3** and corresponding unsaturated polyester from first reaction step before adding poly(ethylene glycol) mono-methyl ether.

ble IV). The combination of all these methods proves that the major fraction of poly(ethylene glycol) mono-methyl ether has been coupled with the carboxyl groups of the polyester.

Curing of Resins Composed of Unsaturated Block Copolymers and Styrene

The block copolymers **2–6** were mixed with styrene (compositions, see Table II) directly after their synthesis. The crosslinking of these resins was studied on a thermal scanning rheometer. The instrument detects viscosity changes by moving up and down a probe that is positioned in the sample. The samples were mixed with 1 wt % of cobalt octoate and 1 wt % of methyl ethyl ketone peroxide. The peroxide is activated by the cobalt octoate in a redox reaction to produce free radicals, which initiate the crosslinking reaction between the styrene monomer and the double bond in the polyester.[3] After addition of the initiator the probe was lowered into the sample and measurement was started at a temperature of 25°C. A typical plot is shown in Figure 7. The solid line describes the storage dynamic viscosity (η') and the dotted line describes the loss dynamic viscosity (η''). The onset of the rapid increase in both viscosities was defined as the gel time of the resin. The results are summarized in Table V. Only the resins **II**, **III**, **VI**, and **VII** containing the short poly(ethylene glycol) segments could be cured in a reasonably short time within less than half an hour. Block copolymer **5**, with the longest poly(ethylene glycol) end group, crystallizes at room temperature. Faster curing is achieved if the

amount of peroxide is increased to 2 wt % methyl ethyl ketone peroxide as seen in a comparison of resins **VI** and **VII**.

DSC Characterization of Cured Resins

The cured samples were analyzed by DSC. DSC experiments will reveal if the sample contains still unreacted styrene monomer and if the poly(ethylene glycol) is phase separated or miscible in the cured resin. For comparison, the resin **I** was cured under the same conditions. The cured product has a T_g around 55°C, which is a typical value for a cured unsaturated polyester of this type.[15] The cured resins containing the block copolymers (resins **II**, **III**, and **IV** with 30 wt % styrene) have lower glass transition temperatures. The glass transition temperature decreases with increasing length of poly(ethylene glycol) segment (Fig. 8), indicating that the poly(ethylene glycol) segment is homogeneously miscible in the cured resin. This is also supported by the fact that in all cases only one glass transition was detectable by DSC. Resin **V** containing block copolymer **5** is phase separated. In addition to the glass transition, an endothermic peak is present at 48°C. This is due to the melting of phase separated poly(ethylene glycol) segments. The exothermic enthalpy values integrated in the temperature range from 100–200°C (Table V) indicate that the curing is almost complete for resins **I**, **II**, **III**, and **V**, whereas the cured resin **IV** contains still residues of styrene. Unreacted styrene will crosslink thermally during the first heating run of the DSC experiment giving rise to an exothermic
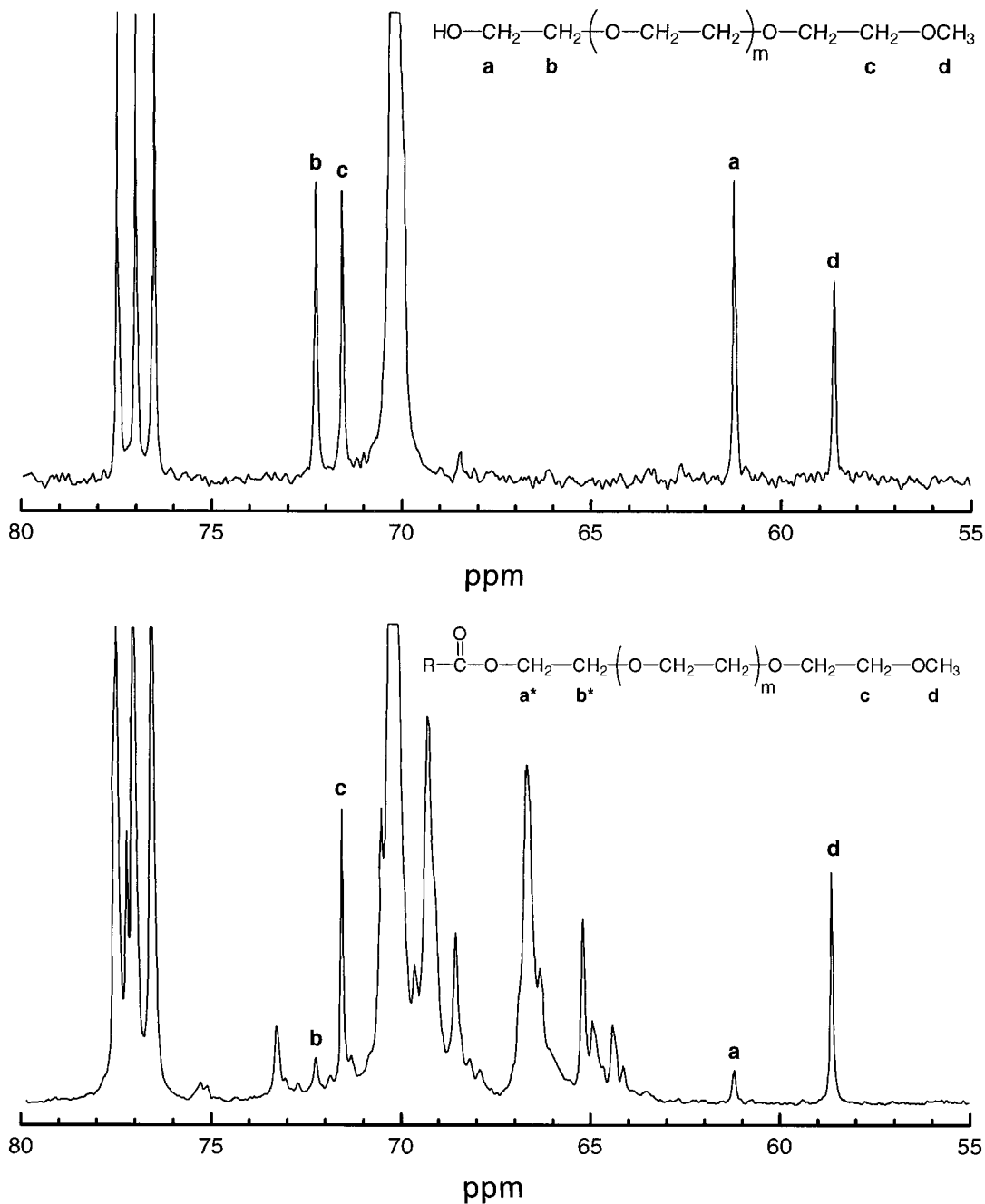
Figure 6 ^{13}C-NMR spectra of (a) block copolymer **4** and (b) unreacted poly(ethylene glycol) mono-methyl ether used in the block copolymer (solvent: CDCl$_3$).

peak. This peak is only observable in the first heating curve and absent in all following heating curves.

Mechanical Properties of Cured Resins

The cured resins **II–IV**, which are based on block copolymers **2–4** were rather soft and flex-ible as the poly(ethylene glycol) end groups act as internal plasticizer. Harder specimens were achieved by increasing the amount of double bonds in the polyester chain. In block copolymers **6** the MA/PA ratio is 2 : 1 and a more densely crosslinked network is formed that results in a harder specimen. The resin **VI**, composed on block copolymer **6** and 20 wt % styrene,

Table IV   Composition of Block Copolymers 2–6

Sample	Content of Poly(ethylene glycol)	
	Calculated[a] (wt %)	Determined by ¹H-NMR (wt %)
2	17.5	17.5
3	27.7	26.4
4	31.9	32.8
5	57.1	53.8
6	22.0	23.3

[a] Calculated for one poly(ethylene glycol) end group per polyester chain.

was, therefore, selected for mechanical testing. Three unreinforced castings (**A**, **B**, and **C**) of this resin were prepared in metal frames (size 100×150 mm) between PET films. Parafin (500 ppm) was aded to the resin in order to reduce the oxygen inhibition of the redox initiated crosslinking reaction.[3] The castings were post-cured for 24 h at 60°C. Four specimen bars of dumbbell type were cut from each casting. The postcuring is important as it completes the crosslinking and removes regions with residual stresses caused by the curing reaction. The stress–strain measurement results are summa-

rized in Table VI. As a reference, an equivalent measurement of a commercial unsaturated polyester resin was done. Both modulus and tensile strength are reduced, compared to the reference, while the elongation is increased. This result is an expected effect of the poly(ethylene glycol) end groups, which are not crosslinked but freely incorporated in the crosslinked resin network. The poly(ethylene glycol) units act as internal plasticizer and reduce the overall crosslink density. Similar results have been achieved by Pandit et al. when using block copolymers of poly(ethylene glycol) and maleic anhydride as compatible reactive impact modifiers for unsaturated polyesters.[8] The unsaturated block copolymer is crosslinked with the unsaturated polyester and the poly(ethylene glycol) segments will remain as free dangling chains in a similar way as the poly(ethylene glycol) end groups. They are uniformly distributed at a molecular level within the base network. The resin samples are, therefore, transparent.

In order to achieve better mechanical properties it is necessary to use incompatible modifiers.[4–8] They remain as domains dispersed in the resin network. The effect on mechanical properties will depend on the morphology of the modifier domain, which in turn, is dependent on the interfacial chemical interactions between the mod-
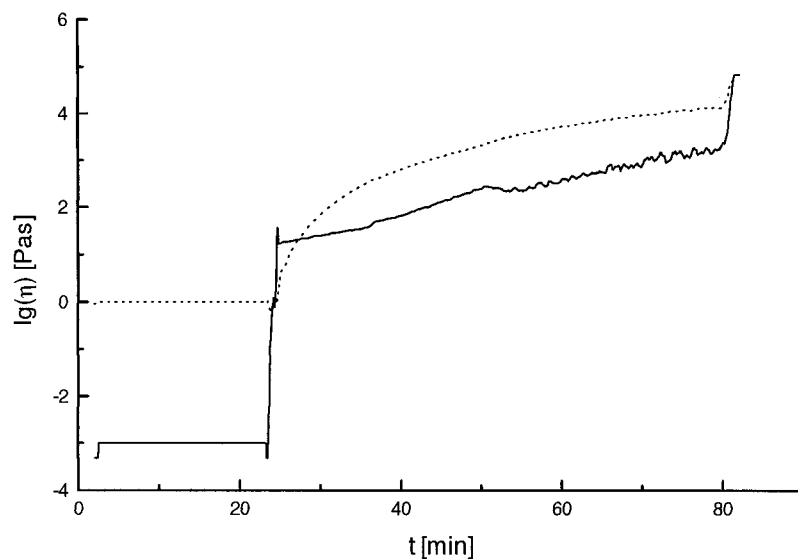

Figure 7 Observation of the curing process of resin **II** with a thermal scanning rheometer at 25°C. Solid line: storage dynamic viscosity, η'; dotted line: loss dynamic viscosity, η''. The onset of the rapid increase in both viscosities was defined as the gel time. The sample contained 30 wt % styrene and was initiated with 1 wt % methyl ethyl ketone peroxide activated with 1 wt % cobalt octoate.

Table V   Curing Behavior and Thermal Properties of Resins I–VII

Sample	Styrene Content (wt %)	Initiator[a] (wt %)	Gel Time (min)	T_g[b] (°C)	ΔH[c] (J/g)
I	30	1	—	50	0
II	30	1	23	19	3
III	30	1	27	−7	1
IV	30	1	—	−12	19
V	30	1	—	−35[d]	0
VI	20	2	9	22	7
VII	40	2	15	58	6

[a] Initiated with 1 or 2 wt % methyl ethyl ketone peroxide and 1 wt % cobalt octoate.
[b] Data from the second heating run.
[c] Data from first heating run; exothermic peak integrated from 100–200°C.
[d] Additional endothermic peak at 48°C.

ifier and the resin matrix. With respect to the uniform dispersion of such modifiers poly(ethylene glycol) end groups in unsaturated polyesters may improve the dispersion of polar fillers and the interfacial properties between filler and matrix.

CONCLUSIONS

It is possible to modify the end groups of unsaturated polyesters with monofunctional poly(ethylene glycol) segments of different molecular weight. The resulting block copolymers have predominantly one poly(ethylene glycol) end group per polyester segment. The solubility in styrene is enhanced allowing the preparation of at room temperature processable resins with a styrene content as low as 20 wt %. The resins can be cured. The glass transition of the cured samples decreases with increasing length of the poly(ethylene glycol) end group.

The mechanical properties of the cured samples range from soft/flexible to hard/brittle, depending on the molecular weight of the poly(ethylene glycol) segment and the styrene content. The synthesized block copolymers may be suitable to uniformly disperse modifiers and improve the interfacial properties between polar fillers and the cured polyester matrix. Experiments along these lines should be performed.
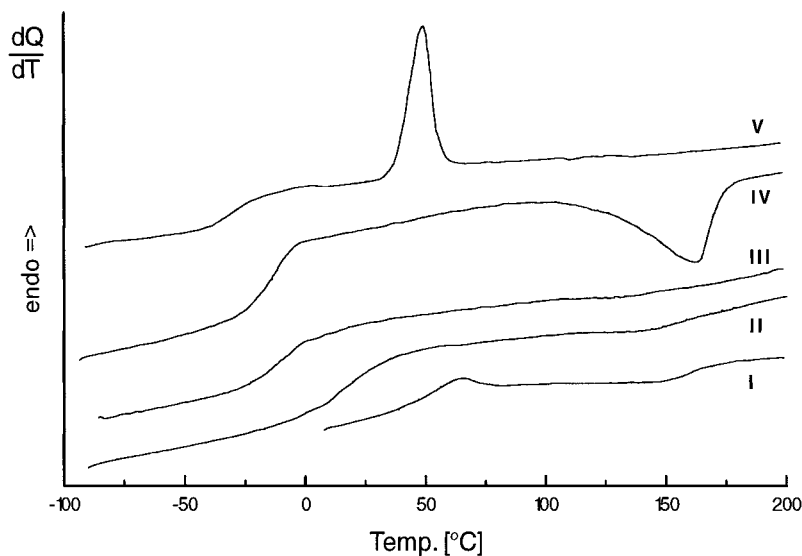

Figure 8   DSC curves of cured resins **I-V** (first heating, heating rate: 10 K/min).

Table VI Mechanical Properties of Three Postcured Castings (A, B, C) of Resin VI (Containing Block Copolymer 6 and 20 wt % Styrene)

Casting	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)
Reference[a]	3000	55	2.0
A	750	15.9	4.0
B	780	13.6	3.1
C	804	12.7	5.3

[a] Data from Neste Polyester, Finland.

REFERENCES

1. J. Makhlouf, in *Encyclopedia of Chemical Technology,* Vol. 18, H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Eds., Wiley, New York, 1983, pp. 575–594.
2. W. E. Douglas and G. Pritchard, in *Developments in Reinforced Plastics,* Vol. 1, G. Pritchard, Ed., Applied Science, London, 1980, pp. 231–255.
3. J. Selley, in *Encyclopedia of Polymer Science and Engineering,* Vol. 12, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. J. Kroschwitz, Eds., Wiley, New York, 1985, pp. 256–290.
4. S. N. Tong, D. S. Chen, and T. K. Kwei, *Polym. Eng. Sci.,* **25,** 54 (1985).
5. S. N. Tong and P. T. K. Wu, *Polym. Plast. Technol. Eng.,* **27,** 519 (1988).
6. S. N. Tong, C. C. Chen, and P. T. K. Wu, *Polym. Mater. Sci. Eng.,* **57,** 785 (1987).
7. S. N. Tong and P. T. K. Wu, *J. Reinforced Plast. Compos.,* **9,** 299 (1990).
8. S. B. Pandit and V. M. Nadkarni, *Ind. Eng. Chem. Res.,* **33,** 2778 (1994).
9. Z.-X. Guo and A. Gandini, *Eur. Polym. J.,* **27,** 1177 (1991).
10. J. P. Agrawal, K. S. Kulkarni, D. V. Wast, M. P. Chouk, and M. M. Marathe, *J. Mater. Sci.,* **27,** 4577 (1992).
11. J. P. Agrawal and K. S. Kulkarni, *J. Appl. Polym. Sci.,* **32,** 5203 (1986).
12. J. P. Agrawal, M. P. Chowk, and R. S. Satpute, *Br. Polym. J.,* **14,** 29 (1982).
13. J. Meixner and W. Kremer, In *Proceedings of 19th FATIPEC Congress,* Vol. 1, xxxxx, xxxxx, 1988, pp. 65–74.
14. G. Odian, *Principles of Polymerization,* Wiley, New York, 1981.