Chemical Modification of Poly(styrene-co-maleic anhydride) with Primary N-Alkylamines by Reactive Extrusion

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SYNOPSIS

Reactive melt-processing of poly(styrene-co-maleic anhydride) (SMA) with primary N-alkylamines was carried out in one step in a twin-screw extruder. Ring formation of the imide occurred within the residence time of the extruder, at temperatures exceeding 220°C and with an excess of primary amines. The increasing chain length of grafted amine onto the SMA backbone depressed the glass transition temperature of poly(styrene-co-N-alkylmaleimides) remarkably. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the past, the reaction of poly(styrene-co-maleic anhydride) (SMA) with primary N-alkylamines has been accomplished in organic solvents at 125°C and pressures between 4×10^5 and 10^6 Pa for 8–48 h.[1,2] Generally, the use of solvents facilitates the control and reactivity between the reactants. Another very attractive approach is to perform this modification by reactive extrusion. In this case, the main medium is the molten polymer and the reaction and process parameters are very different, especially temperature and viscosity. The process of reacting SMA with primary amines in the melt in a twin-screw extruder has some advantages over the conventional reaction in solution[3,4]: (i) the absence of solvents leads to savings in raw materials and solvent-recovery systems; (ii) high amounts of the reacted species can be obtained since extruders can handle high-viscosity polymers; (iii) the reaction kinetics can be accelerated as the reactions can be conducted over a large range of temperatures (70–500°C) and pressures (0–507 × 10^5 Pa); and (iv) continuous production of ready-to-use materials is possible. Limitations of reactive extrusion, however, are (i) the high processing temperatures that can lead to side, oxidation, or degradation reactions; (ii) the lowered solubility of coreagents; and (iii) the delayed diffusion of reagents in the polymer melt.

Moore et al.[5] described the reaction of SMA with N-alkylamines in methyl ethyl ketone at 25°C, after which the aminated copolymer was melt-processed for 30 min on a two-roll mill at 170°C and further devolatized by heating at 213°C for 4 h under vacuum. Lambla[6] obtained imidized copolymers from SMA by previous treatment of the SMA with gaseous ammonia for 6 h and subsequent melt-processing in a single-screw extruder. By this two-step process, imide conversion levels of 78% were obtained for a screw speed of 20 rpm. Bourland et al.[7] and Song and Baker[8] studied the relative reactivity of primary, secondary, and tertiary amines and diamines toward carboxylic acid and anhydride groups in polymers in the melt. The imidization reaction, however, also consisted of a two-step process.

In this article, a much more attractive, time-saving, and cost-reducing method is represented whereby the SMA is reacted with primary amines in a corotating twin-screw extruder in one step within reaction times of 3 min. For all amines used, except for ammonia, almost complete imidization was obtained within the residence time of the extruder.
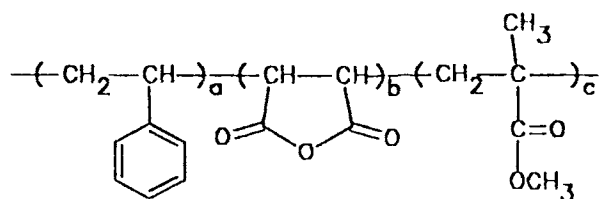

Figure 1 Schematic representation of an SMA copolymer containing (a) styrene, (b) maleic anhydride, and (c) methyl methacrylate.

EXPERIMENTAL

A commercial SMA (Monsanto EX 3600) containing 25 wt % maleic anhydride (MA), 7 wt % methyl methacrylate (MMA), and 68 wt % styrene (Sty) with an intrinsic viscosity of 0.43 was used in this study (Fig. 1). Ammonia (25% aqueous solution) from Baker and methylamine (40% aqueous solution), ethylamine, propylamine, butylamine, hexylamine, and dodecylamine (99%) from Janssen were used without further purification.

The imidization reaction of MA groups of SMA with primary amines (Fig. 2) was carried out in a Leistritz corotating twin-screw extruder with 10 barrels of 22 cm length each (Fig. 3). The external screw diameter was 34 mm. The SMA pellet feeder and the primary amine dosage pump were calibrated prior to use in order to determine the input of SMA and amine required for the reaction. A LEWA EKM 1612 dosage pump was connected to barrel 4 of the extruder and allowed introduction of the primary amine solution through two injection ports, separated about 10 cm from each other. The pressure of amine injected in the melt was maintained at 32

$\times$ 10^5 Pa during the extrusion. The flow rate of amine under this pressure at various stroke lengths is given in Table I. Within every stop of the extruder, a recalibration of the dosage pump was necessary because blockage of the injection ports at barrel 4 with molten polymer could reduce the output of amine to the extruder considerably, which was not desired.

Glass transition temperatures (T_g) were measured on a Perkin-Elmer DSC-7 at a heating rate of 10°C/min; the second run was used to determine the T_g. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM 250 from deuterated THF-d8 solutions at 60°C, a frequency of 62.9 MHz (^{13}C), and a scan amount of 21,728. ^{1}H-NMR scans were obtained at 60°C from a deuterated THF-d8 solution on a 250 MHz instrument. FTIR was performed on a Bruker IFS 66 at a resolution of 2 cm^{-1}, a minimum of 16 scans were signal averaged, and the spectra were stored on a magnetic disk. Polymer films for FTIR analysis were prepared by solution casting onto KBr windows from a 2% (w/v) solution in anhydrous THF. The films were dried in a vacuum oven at 80°C for one night and stored in a desiccator prior to use. The maleimide content in the copolymer was determined by elemental nitrogen analysis and titration of residual MA groups.[9] The chemiluminescent nitrogen analyzer involves an oxidative pyrolysis of the resin converting all chemically bound nitrogen into nitric oxide. The nitric oxide is then reacted with ozone to produce a metastable nitrogen dioxide that chemiluminescences as it relaxes. The chemiluminescence is sensed by a photomultiplier tube, amplified, and displayed. The titration analysis consists of dissolving the polymer in pyridine, adding
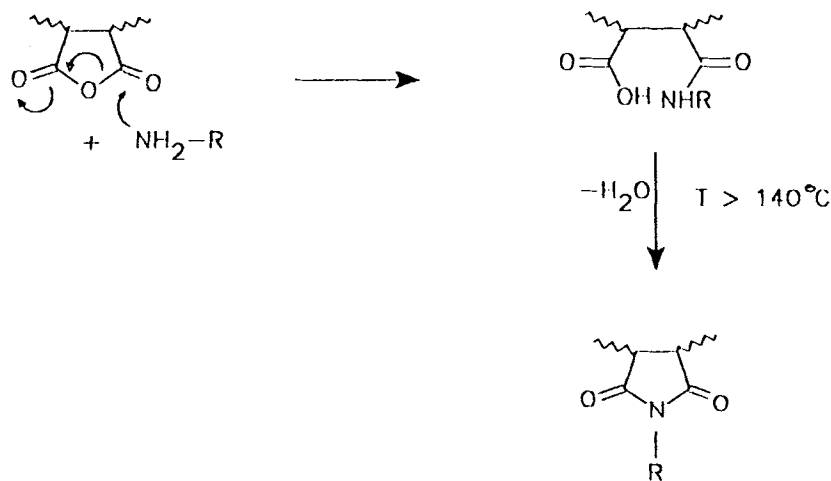

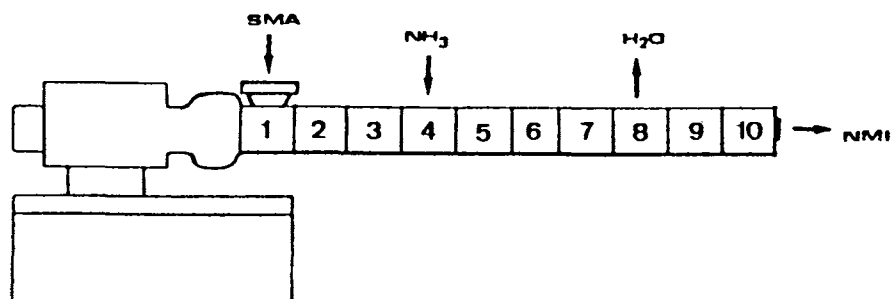**Figure 2** Schematic representation of the imidization reaction.

Figure 3 Schematic representation of the twin-screw extruder setup.

distilled water to hydrolyze the MA to maleic acid, and titrating it to a thymol blue endpoint. Both analyses were run in triplicate.

RESULTS AND DISCUSSION

Synthesis of Poly(styrene-co-N-alkylmaleimides) as Obtained from Imidization of Poly(styrene-co-maleic anhydride) by Reactive Extrusion

The imidization reaction was performed in a Leistritz corotating twin-screw extruder containing 10 barrels, each being heated at varying temperatures (240–265°C) (Table II). The SMA polymer, poured into barrel 1 and molten in barrels 2 and 3, was reacted with primary N-alkylamine in barrels 4–7, being the reaction zone. The primary N-alkylamine solution, injected under high pressure into the polymer matrix, was added in excess of at least 2 mol amine compared to anhydride, except for the poly(styrene-co-N-dodecylmaleimide), which was added as a solid.

The screw design, conceived especially for the imidization reaction, contained not only kneading, conveying, and intensive mixing elements, but also reverse elements (barrels 3 and 7), allowing the molten polymer mass to convey into the opposite direction to increase the reaction time and reaction surface. After reaction in barrels 4–7, the imidized SMA was conducted through a sealed venting chamber mounted onto the extruder on barrel 8 in order to eliminate the water of condensation and excess of amine. A vacuum of minimum 0.6×10^5 Pa was maintained during the extrusion. The distillation of the condensation water by this means appeared to be very important with respect to the conversion level. Bourland et al.[7] described the imidization kinetics in solution to be determined by the cyclization of the amide–acid. The equilibrium

of this reaction is thus directed toward the side of imide formation in the presence of excess of primary N-alkylamine, at a temperature exceeding 140°C and with elimination of the condensation water. It can be observed that this is also true for imidization occurring in the molten state. After extrusion, the imide polymer was drawn into hot water to prevent breaking up and was chopped into pellets. The pellets were then dried overnight in a vacuum oven.

Table I   Calibration Data of the SMA Pellet Feeder and the Amine Dosage Pump

Calibration of the SMA Pellet Feeder at a Screw Rate of 100 rpm	
Stroke Length (mm)	Output (g/5 Min)
10	230
11	251
12	283
13	320
14	350
15	380
17	444
20	556
25	706
30	858

Calibration of the Dosage Pump Drive Unit with Ammonia	
Stroke Length (mm)	Flow Rate (mL/5 Min)
15	65
12	49
9	33
6	16

Table II   Operating Conditions of the Twin-screw Extruder

| Type | Temperature Profile of the Barrels (°C) | | | | | | | | | | Input Amine (g/5 Min) | Input SMA (g/5 Min) |
	Die	9	8	7	6	5	4	3	2	1		
NMI	250	260	265	265	265	265	260	250	250	240	45	120
NMMI	230	230	240	250	255	255	255	255	250	240	45	120
NEMI	230	230	240	250	255	255	255	255	250	240	40	121
NPrMI	230	230	240	250	255	255	255	255	250	240	36	120
NBMI	230	230	240	250	255	255	255	255	250	240	37	126
NHMI	220	220	220	220	240	240	240	240	240	230	38	120
NDMI	150	150	155	180	210	220	220	220	220	220	45	120

Abbreviations used: NMI, poly(styrene-co-N-maleimide) derived from ammonia; NMMI, poly(styrene-co-N-methylmaleimide); NEMI, poly(styrene-co-N-ethylmaleimide); NPrMI, poly(styrene-co-N-propylmaleimide); NHMI, poly(styrene-co-N-hexylmaleimide); NDMI, poly(styrene-co-N-dodecylmaleimide).

This extremely easy process enabled us to obtain amidation and cyclization in one step at high conversion yields in a continuous way. No catalyst, solvent, stabilizer, or processing agents were added. It has to be noted that samples with the same imide level were obtained after operating under identical conditions.

Molecular Characterization of Poly(styrene-co-N-alkylmaleimides)

Characterization of the various poly(styrene-co-N-alkylmaleimides) on their imide content was performed by elemental nitrogen analysis and titration of nonreacted MA groups. From Table III, it can be derived that conversion levels of almost 100% were reached for all poly(styrene-co-N-alkylmaleimides),

except for NMI; the lower conversion level obtained for NMI (85%) is considered to result mainly from the presence of water and its effect on the imidization kinetics. Of all primary amines, ammonia is used as a 25% solution, whereas all other amines are 99% solutions (except for methylamine: 40%).

GPC (styrene-co-divinylbenzene columns) measurements performed on the poly(styrene-co-N-alkylmaleimides) in THF exhibit a systematic increase in molecular weight for polymers containing longer side chains. This observation clearly indicates that degradation or chain scission of the SMA polymer backbone did not occur, or at least not extensively, during extrusion.[10] The molecular weight distribution remains constant and relatively narrow.

From DSC experiments at a scanning rate of 10°C/min, the glass transition temperature was de-

Table III   Characterization of the Various Poly(styrene-co-N-alkylmaleimides

| Samples | Conversion (%) | | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | T_g (°C)[a] |
	Titration	Elemental N			
SMA			[b]	[b]	153
NMI	[c]	85	[b]	[b]	173
NMMI	97	97	95,000	1.88	151
NEMI	97	92	97,000	1.85	144
NPrMI	97	96	101,600	1.91	135
NBMI	97	94	114,500	1.86	126
NHMI	97	97	122,600	1.92	100
NDMI	[d]	95	145,400	1.88	

[a] DSC scanning rate of 10°C/min.
[b] Interaction of the polymer with Styragel column.
[c] Acidic NH will react with MeOH/NaOH.
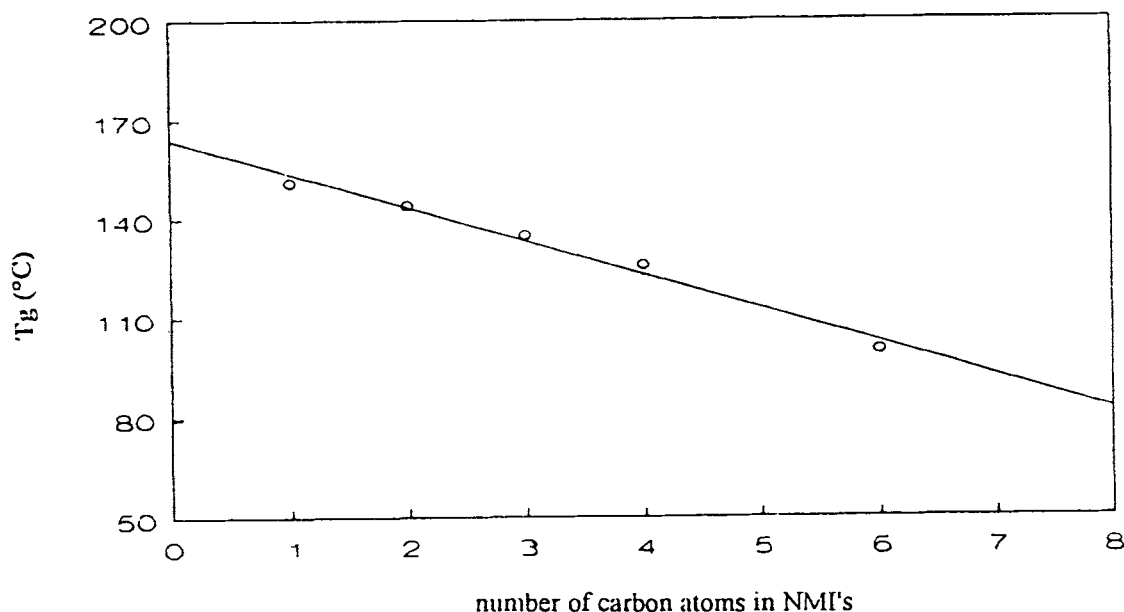[d] Non-solubility of NDMI in pyridine/NaOH.

Figure 4 T_g vs. the amount of carbon atoms in the N-alkyl side group of maleimide based-polymers.

rived and plotted as a function of the number of carbon atoms in the N-alkyl side chain (Fig. 4). A monotonic decrease in T_g is observed with an increase in length of the flexible N-alkyl side chain. This is also reflected in the temperature profile of the barrels; upon increasing the chain length of the N-alkyl group, the viscosity of the polymers decreased considerably due to the internal plasticization such that we had to decrease the barrel temperatures. This phenomenon, caused by an increasing free volume with reduced packing density and consequent reduction in steric hindrance to segmental mobility continuous until a critical side-chain length is reached.[11-13] If, for instance, we assume, for practical reasons, a linear relationship between T_g and the number of carbon atoms in the side chain, then T_g (°C) = 164 (°C) − 10.2× (number of carbon atoms in the side chain). From all the poly(styrene-co-N-alkylmaleimides) studied, the T_g of NMI derived from ammonia by this relation and conversion degree of 95% was found to be 164°C (Fig. 4). Experimentally, a T_g of 173°C was obtained for a 85% conversion level of imidization in SMA. It is believed that the presence of hydrogen bonds between the carbonyl and the NH groups of maleimide is responsible for the increased T_g of the ammonia-derived NMI.[14]

NMR and FTIR analysis of the products indicated that an imide ring was formed in the absence of amide or acid groups. A ^{13}C-NMR spectrum of

the NMI compared to its parent SMA shows a shift of the carbonyl from 173 to 179.6 ppm; this is consistent with the substitution of the MA by the maleimide (Fig. 5). The downfield shift of the imide carbonyl compared to the anhydride is due to the larger electronegativity of the oxygen atom in the cyclic ring.[15] In the ^{1}H-NMR spectrum, only a minor change in the polymer backbone is observed; a broad peak at 9.4 ppm is observed corresponding to the imide proton (Fig. 6). The sharp peaks in the low-field region are ascribed as resulting from deuterated THF.

Figure 7(A) represents the FTIR spectrum of SMA. The main vibrational bands of MA in SMA are located at 3630 cm^{-1} (2× $\nu_{C=O}$), 1858 cm^{-1} (in-phase $\nu_{C=O}$), and 1779 cm^{-1} (out-of-phase $\nu_{C=O}$). An additional vibration band for the carbonyl stretching of MMA (7 wt %) is observed at 1725 cm^{-1} in the spectrum of SMA. In the FTIR spectrum of NMI [Fig. 7(B)], new broad bands are being observed in the 3500–3000 cm^{-1} region, attributed to the NH stretching of maleimide units. Upon imidization, a decrease in intensity for the absorption bands of the carbonyl groups of MA groups at 1858 and 1779 cm^{-1} is observed [Fig. 8(A)] with the appearance of new bands at 1779 and 1716 cm^{-1}, attributed to the in- and out-of-phase carbonyl stretching vibration modes of maleimide [Fig. 8(B)]. In the fingerprint region, two bands at 1346 and 1180 cm^{-1} are observed and attributed to the
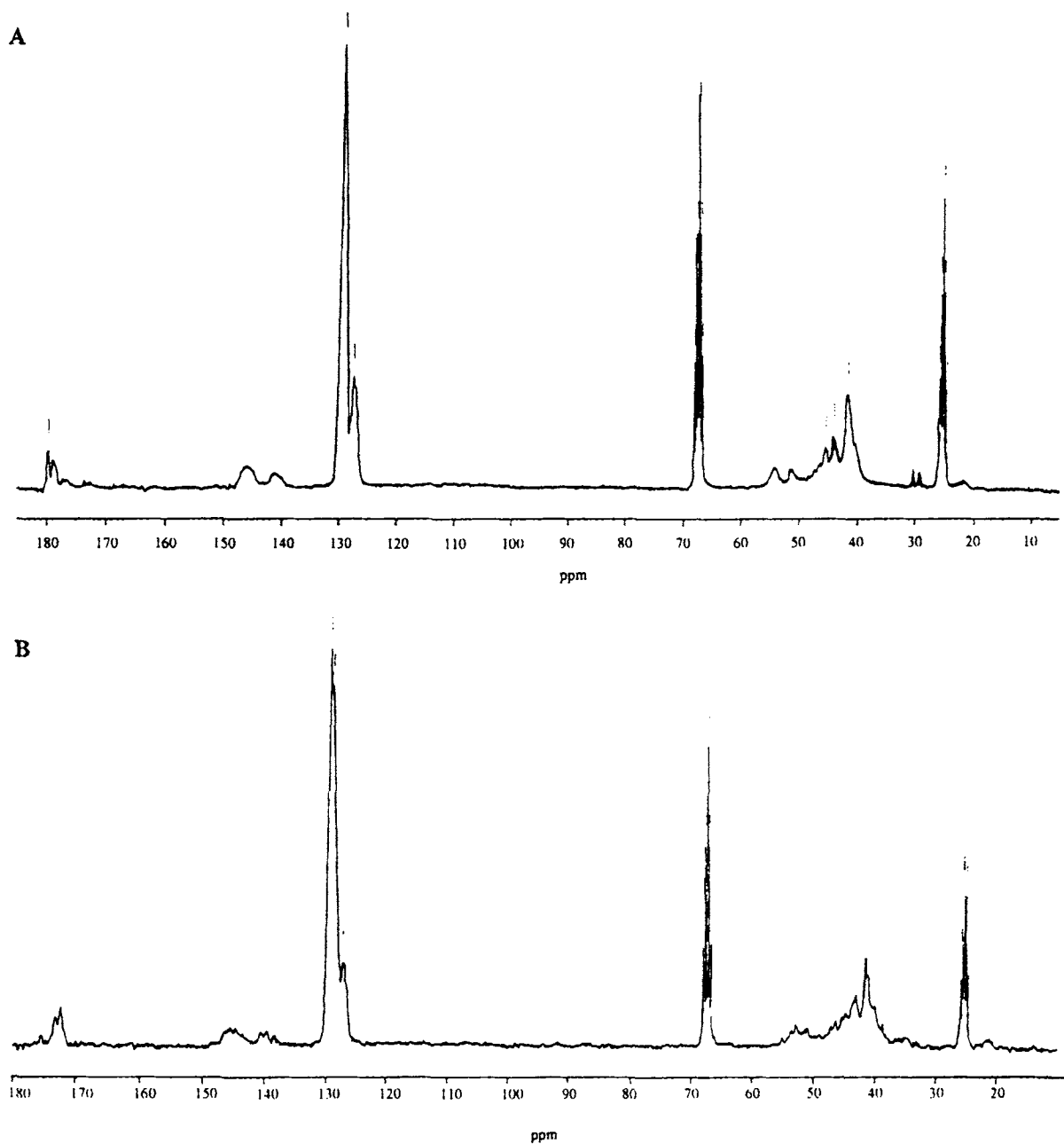
Figure 5 ^{13}C-NMR spectrum of (A) NMI and (B) SMA.

NH bending and C — N — C stretching of the ma-leimide groups (Fig. 7). As is usually indicated by "potential energy distortion" calculations, both motions are coupled to each other.

The vibration modes of the maleimide units are consistent with those found in the literature for low molecular weight compounds.[16-19] From the FTIR spectra, one can conclude that no amide or acid groups are present in the NMI copolymer. Snyder

et al.[20,21] reported amide–acid vibrational modes to be characterized by two bands in the 1800–1600 cm^{-1} region: a mode near 1700 cm^{-1} that is assigned to hydrogen-bonded carboxylic acid pairs and a mode near 1660 cm^{-1} assigned to hydrogen-bonded amide groups. Since none of these show the carbonyl stretching region of the FTIR spectrum of NMI, we may conclude that the ring opening of the anhydride and the cyclization of the amide–acid occurred
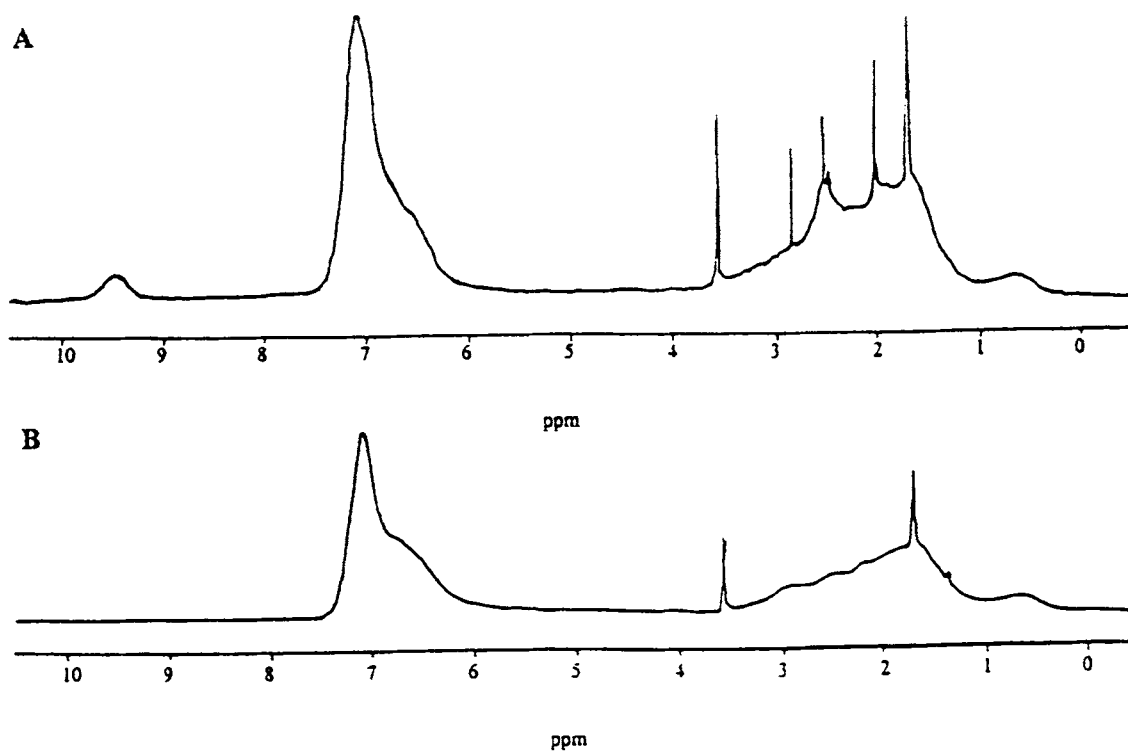
A

ppm

B

ppm

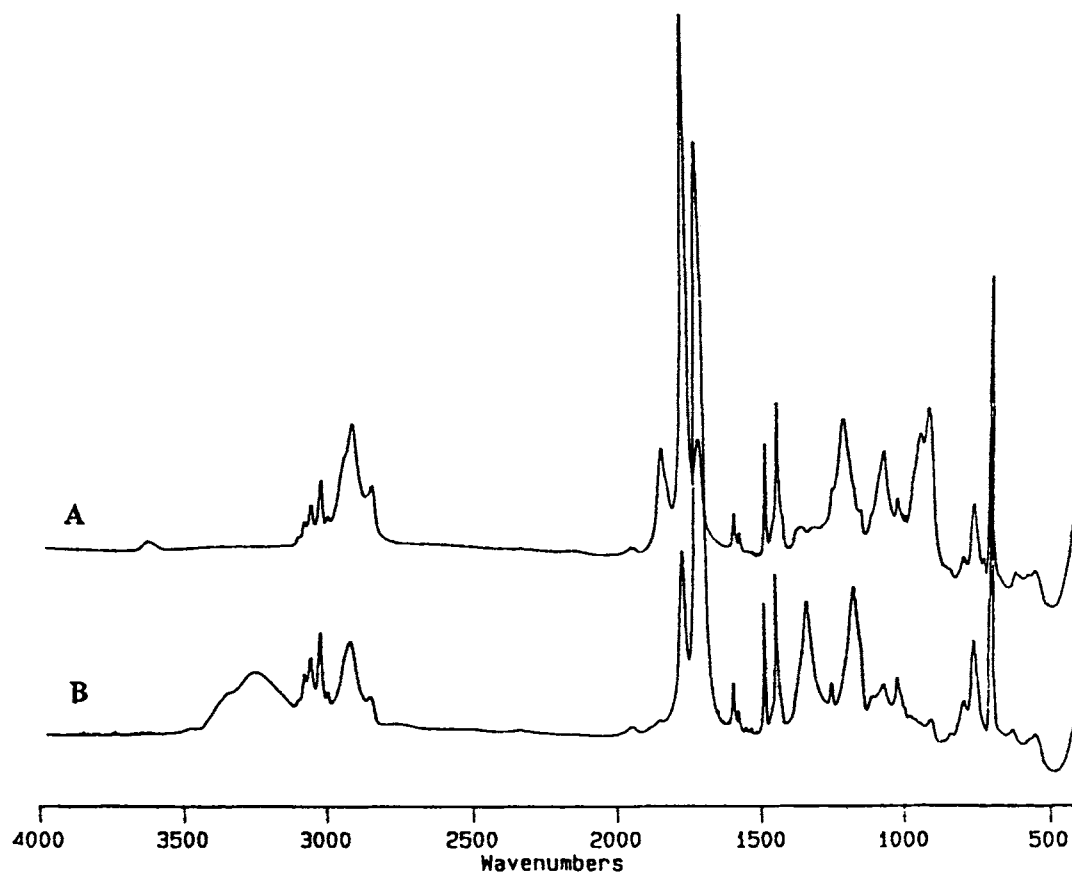**Figure 6** ¹H-NMR spectrum of (A) NMI and (B) SMA.

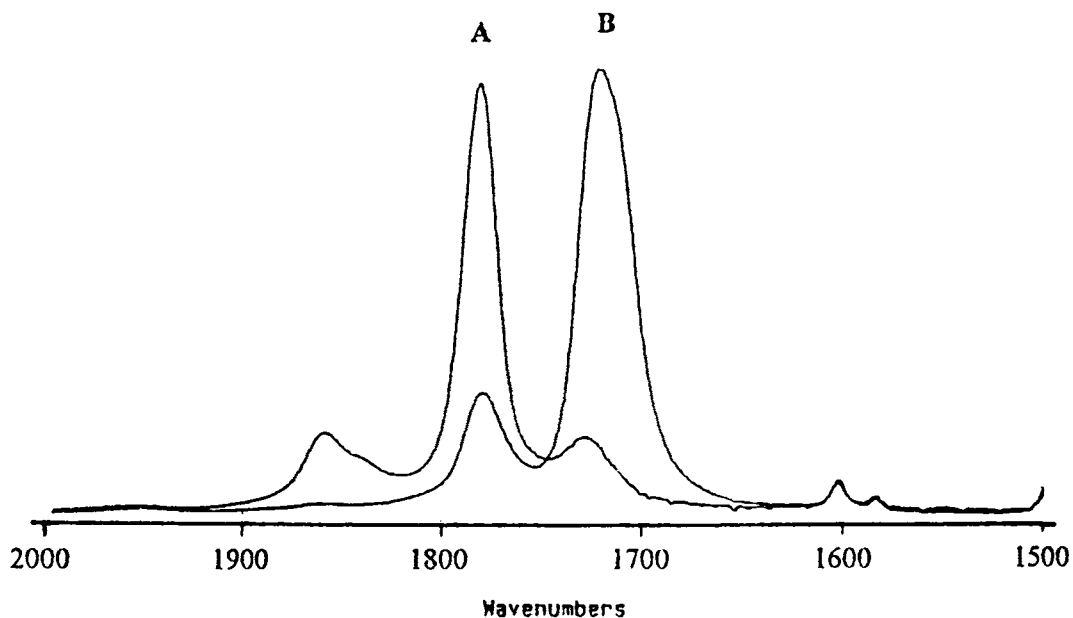**Figure 7** FTIR spectrum of (A) SMA and (B) NMI.

Figure 8 FTIR spectrum of the carbonyl region of (A) SMA and (B) NMI.

within the residence time of the extruder. Methyl substitution of the acidic NH blocks the association and this is experimentally confirmed by the FTIR spectrum of NMMI; no bands were observed in the 3500–3100 cm^{-1} region, indicating no hydrogen bonds to be present (Fig. 9).
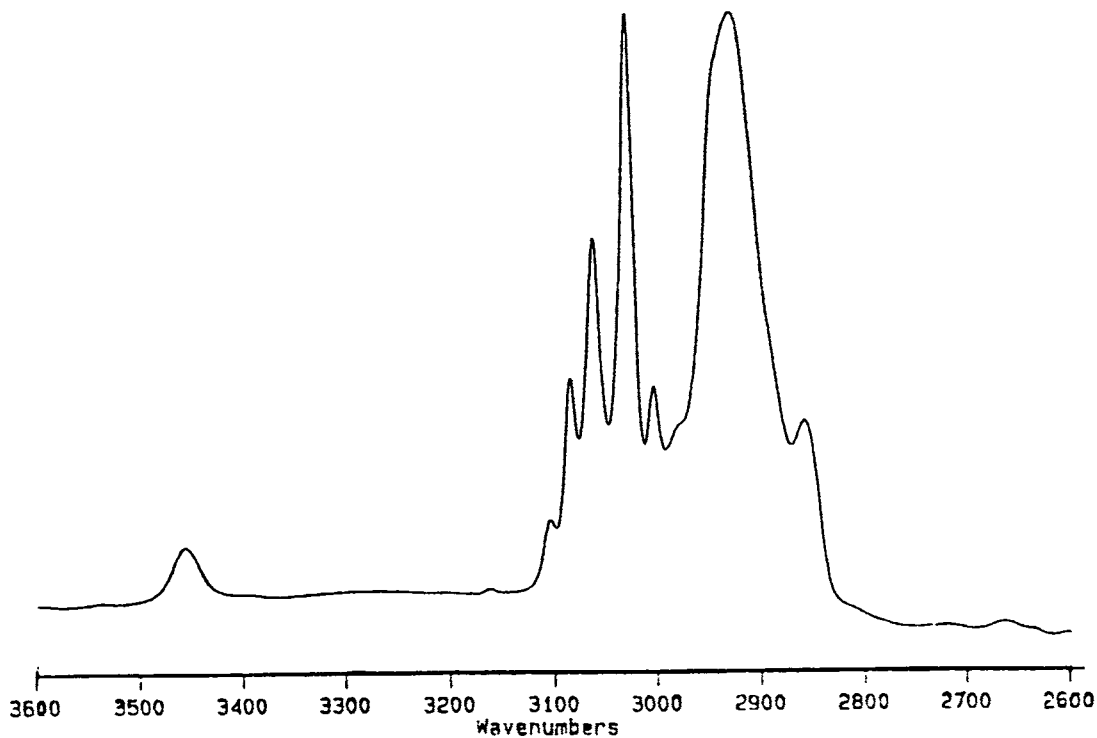

Figure 9 FTIR spectrum of the NH region of NMMI.

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CONCLUSIONS

From our experiments, it can be derived that poly(styrene-co-maleic anhydride) has been modified successfully with primary N-alkylamines in a one-step extrusion process within reaction times of 2–7 min at temperatures exceeding 220°C. By using vacuum vents to remove the water byproduct eliminated during the ring closure, almost complete imidization of the SMA was accomplished during the residence time of the extruder. From FTIR spectroscopy of the NMI copolymer, no acid–amide groups were detected, indicating the two steps of the imidization reaction to be complete. Grafting primary amines of increasing chain length onto the SMA copolymer depressed the glass transition temperature of the poly(styrene-co-N-alkylmaleimide). Grafting of the ammonia did not result in completely imidized copolymers because of the competition between the water and ammonia for reaction with the anhydride.

I. V. gratefully acknowledges the IWONL and NFWO scholarships. The authors are also indebted to the Monsanto Europe technical center, Louvain-la-Neuve, for the financial support and for the use of the reactive extrusion facilities.

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Received September 14, 1993
Accepted March 25, 1994