

Synthesis of Chloral Derivative of Maleimide and Its Copolymerization with Styrene

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SYNOPSIS

A new monomer *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide (MI) and its copolymer with styrene have been developed. It was found that MI can be synthesized from *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide in acetic anhydride with a yield of 65%. The radical copolymerization of MI with styrene in benzene solution occurs with a yield of 91%. The obtained copolymer has a melting point about 215°C, good thermal resistance, and is self-extinguishing. The monomer and copolymer compositions were determined by elementary, ¹H-NMR and IR analysis.

INTRODUCTION

In some cases the properties of traditional mass plastics can be improved by copolymerization with maleimides. In this way, for instance, it is possible to improve hardness, water absorption, and heat resistance of the polymer materials.¹⁻⁸

Maleimides can be obtained from monomaleamides in dehydration reactions using the dehydrating agents such as acetic anhydride, phosphorus pentoxide, acetyl chloride, and thionyl chloride. This study describes the reaction in the presence of acetic anhydride. The rate of maleimide formation depends, among other things, on the kind of substituent at the nitrogen atom in maleamide. Imidization occurs with a higher yield and without side reactions if the substituent is rather large, rigid, and has electron donor character.^{9,10}

On the other hand it is well-known that there is a possibility to improve also fire resistance of polymers by inserting halogen atoms into the polymer structure. Thus a question arises whether combining an imide group and halogen atoms in one macromolecular structure would combine their influences to obtain a polymer with good thermal stability and fire resistance.

A compound that, under some conditions, can be substituted at nitrogen atoms in maleamides is chloral. It is rigid, has a big molecular mass, and, containing three chlorine atoms, is a good source of halogen.

In our previous works we have found that monomaleamide reacts with chloral¹¹ and that the product of the reaction, *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide, copolymerizes with styrene.¹²

The present work aims at studying the effect of 1-hydroxy-2,2,2-trichloroethyl substituent at nitrogen atoms in monomaleamide on closing of imide rings and ability of *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide to copolymerize with styrene. Interest was focused on the thermal and fire resistance of the copolymer as well.

EXPERIMENTAL

Synthesis

Monomaleamide (MA)

In a well-stirred and ice-cooled concentrated aqueous solution of NH₄OH (containing 1 mol NH₃), 49 g (0.5 mol) maleic anhydride were dissolved slowly. Then 20% solution of HCl was added dropwise until the pH of the reaction mixture was about 4. The crude product was filtered and recrystallized from ethanol and dried. The yield was 70%.

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***N*-(1-Hydroxy-2,2,2-Trichloroethyl)maleamide (ChlMA)**

Monomaleamide [11.5 g (0.1 mol)] and concentrated HCl (0.5 cm³) were added to 147 g (1 mol) chloral. The reaction mixture was stirred and refluxed for 4 h and left overnight in a cold place (about 4°C). A yellow solid was separated out and added to 50 cm³ acetone. The insoluble part was filtered off (it is unreacted monomaleamide), and the solution was concentrated under reduced pressure and cooled. Precipitated crystals were filtered and dried. The yield was 30%.

***N*-(1-Acetoxy-2,2,2-Trichloroethyl)maleimide (MI)**

Anhydrous sodium acetate [5 g (0.1 mol)] was heated for half an hour at 60°C in 50 cm³ acetic anhydride. Then 26.2 g (0.1 mol) *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide was added and the reaction solution was refluxed for 2.5 h. After cooling, the solution was poured into 300 cm³ ice-cold water and well-stirred for 2 h. The precipitate was filtered off and purified by crystallization from ethanol. The yield was 65%.

Copolymer [Styrene-co-N-(1-Acetoxy-2,2,2-Trichloroethyl)maleimide] (StMI)

Styrene, [10.4 g (0.1 mol)], 28.7 g (0.1 mol) *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide, and 0.3 g 1,1'-azobisisobutyronitrile (AIBN) were dissolved in 360 cm³ benzene and refluxed for 10 h. After cooling, the reaction solution was poured into 1.5 L well-stirred and cooled ethanol. The copolymer was filtered and purified by dissolving in benzene and reprecipitation in ethanol. The yield was 91%.

Measurements

IR spectra in KBr disks were run on a Spekord IR-71 spectrophotometer. ¹H-NMR spectra were obtained in DMSO by a Tesla 35-478 spectrometer at 100 MHz. The contents of carbon and hydrogen were determined according to the Knobloch method. The nitrogen content was determined by using the Pregl-Dumas method. The chlorine content was determined by using the Discherl method. Acidity of the products was determined by titration of solutions of samples by 0.1N NaOH. Thermal analysis was done on a Paulik-Paulik C derivatograph under the following conditions: heating rate 10 deg min⁻¹, sample mass 10 mg, argon atmosphere. The melting points were measured by using Boethius apparatus. Fire resistance of copolymer was determined by the test for flammability of plastics materials UL 94.

RESULTS AND DISCUSSION

The conditions under which the investigated reactions were carried out are given in the experimental section. Table I shows the selected properties of the products and yields in which they were obtained.

Compositional Studies

Compositions and structures of the copolymer StMI and intermediate products were determined by using IR (Figs. 1 and 3), ¹H-NMR (Fig. 2), and elemental analysis (Table II).

IR and ¹H-NMR analysis show distinct differences in the structures of the compounds obtained one from the other. A very obvious difference between the IR spectra of ChlMA and MI is at 3100

Table I Selected Properties of the Obtained Compounds and Yields in which They Were Synthesized^a

Property	MA	ChlMA	MI	StMI
Acidity calculated (mg KOH/g)	487.9	213.7	0	0
Acidity found (mg KOH/g)	461.1	225.0	35	17
Melting point (°C)	166–168	145	112	215–219
Soluble in:	H ₂ O, xylene, ethyl acetate	Acetone, DMFA, cyclohexanone	Benzene, CCl ₄	Benzene, CCl ₄ , xylene
Insoluble in:	Benzene, CCl ₄	Benzene, CCl ₄ , THF	H ₂ O	C ₂ H ₅ OH, H ₂ O
Yield (%)	70	30	65	91

^a Abbreviations: MA, monomaleamide; ChlMA, *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide; MI, *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide; StMI, – copolymer [styrene-co-*N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide].

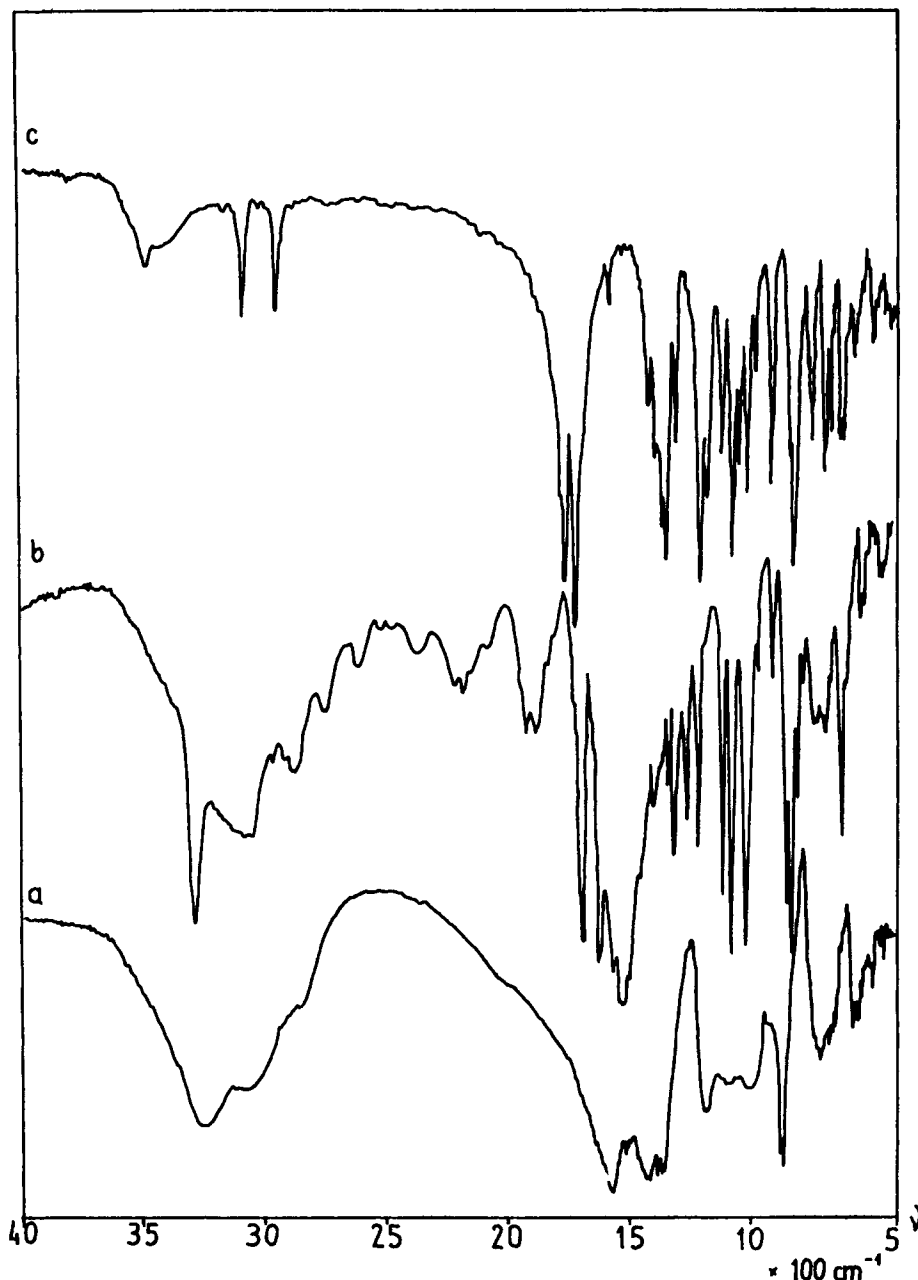


Figure 1 IR spectra of (a) monomaleamide, (b) *N*-(1-hydroxy-2,2,2-trichloroethyl) maleamide, and (c) *N*-(1-acetoxy-2,2,2-trichloroethyl) maleamide.

cm^{-1} , which is a characteristic absorption range of N-H bands in amides. In the IR spectrum of MI the band disappeared, indicating that there are no protons at nitrogen atoms in the structure of MI. The broad bands appearing at $2500\text{--}3300\text{ cm}^{-1}$ in the spectrum of ChlMA could be due to vibration of —OH in carboxyl groups, and the peaks in the ranges $3200\text{--}3400$, $1260\text{--}1350$, and $1030\text{--}1125\text{ cm}^{-1}$ to hydroxy groups in alcohols. In the spectrum of MI these bands are absent. In the spectrum of MI

new bands at 2950 , 1180 , and 1200 cm^{-1} are observed. The first one could be due to —CH_3 absorption and the others to C-O vibration in acetates. These results strongly suggest that during heating of ChlMA in acetic anhydride two reactions occur: closing of imide rings and esterification of hydroxy group from chloral substituent. The spectrum of MI is fairly clear so it is also possible to distinguish the band at 750 cm^{-1} due to —CCl_3 group.

On the other hand, all three spectra show char-

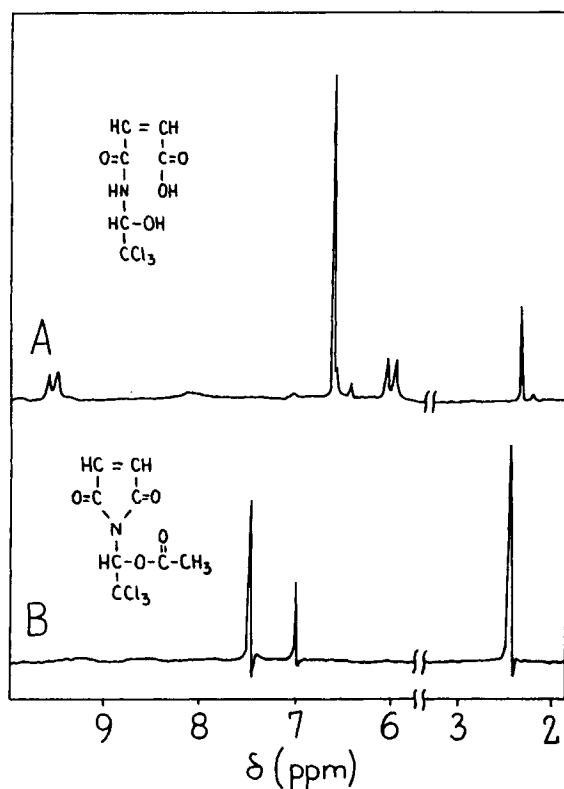


Figure 2 $^1\text{H-NMR}$ spectra of (a) *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide and (b) *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide.

acteristic peaks for the vibrations in $\text{RHC}=\text{CHR}$ group: in the range $3000\text{--}3100$, 1420 , and $695\text{--}670$ cm^{-1} assigned to C-H vibration, and in the range 1580 cm^{-1} attributed to absorption of double-bond $\text{C}=\text{C}$ connected with $\text{C}=\text{O}$. The strong absorption of amide $\text{C}=\text{O}$ vibration is observed: in the MA spectrum at 1580 cm^{-1} , in ChlMA at 1570 , 1530 , 610 cm^{-1} , and in MI at 1770 and 1720 cm^{-1} (Fig. 3).

The spectrum of copolymer StMI is almost a combination of polystyrene and MI spectra. Only the band attributed to vibration of double bonds is absent.

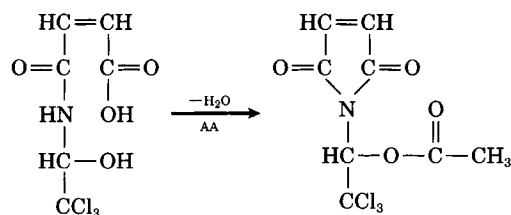
The changes in the structures of investigated compounds are confirmed by $^1\text{H-NMR}$ spectra of ChlMA and MI (Fig. 2). From the spectrum of ChlMA the peaks may be assigned as follows: $\delta = 2.32$ ppm $-\text{OH}$ (alcoholic); $\delta = 6.0$ ppm doublet of methine proton coupled with the proton in amide group; $\delta = 6.6$ ppm two protons at carbons linked by double bond; the broad peak at $\delta = 8.1$ ppm is probably due to $-\text{OH}$ (carboxylic); and the double signal at $\delta = 9.55$ ppm to the amide proton coupled with the proton of the methine group. The $^1\text{H-NMR}$

spectrum of MI shows only three singlets: at $\delta = 2.41$, 6.99 , and 7.42 ppm. The proportion between the integration values of them are $3 : 1 : 2$. The first peak can be assigned to the three protons of methyl group, the second one to methine proton, and the third singlet to two olefinic protons. In the spectrum of MI the peaks of amide proton and carboxylic acid proton disappeared, indicating the ring closure.

In the MI spectrum the peak due to protons of methyl group replaced the signal of alcoholic proton in the spectrum of ChlMA. It confirms the esterification process.

Reactions

On the basis of the spectroscopic and elemental analysis (Table II), which agree with each other, it is possible to state that during heating of *N*-(1-hydroxy-2,2,2-trichloroethyl)maleamide in acetic anhydride (AA) its imidization and esterification of hydroxy group of chloral substituent occur. The product of the reaction is *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide. Its structure and the reaction are shown in the following scheme:



The results of the present investigation prove that *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide copolymerizes easily with styrene in a radically initiated reaction in solution. The elemental analysis may suggest that it is an alternating copolymer. The alternating copolymerization of electron-poor comonomers, such as *N*-substituted maleimides, with electron-rich comonomers, such as styrene, has been well documented.¹³⁻²¹ Deviation from the alternation was observed in reactions carried out in relatively strong donor solvent—ethyl ketone.²²

The alternating copolymerization behavior of these electron-rich and electron-poor comonomers is assumed to arise from a precomplex of the comonomer pair or from a preference of a terminal radical for a monomer of opposite polarizability.²²⁻²⁷

So it may be assumed that *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide can participate in this type of copolymerization process.

The copolymerization and the structure of the copolymer may be presented by the following scheme:

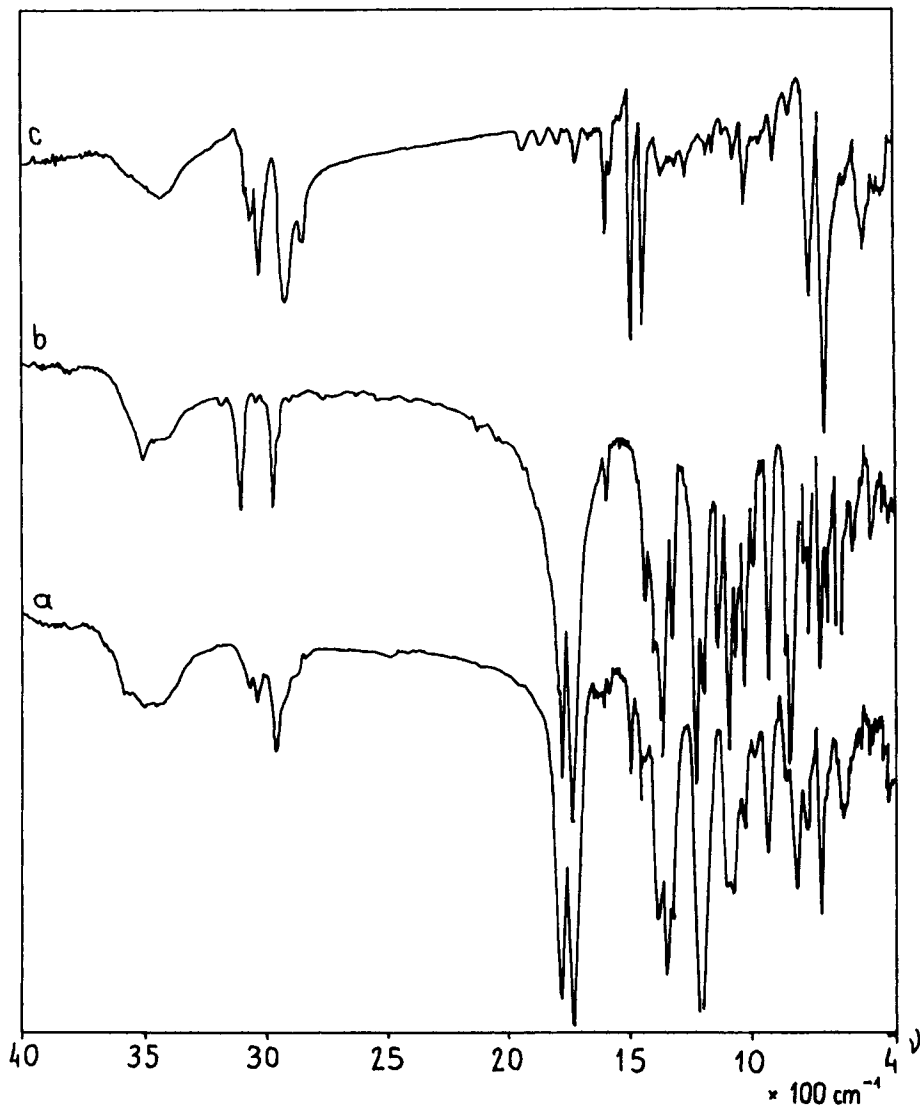
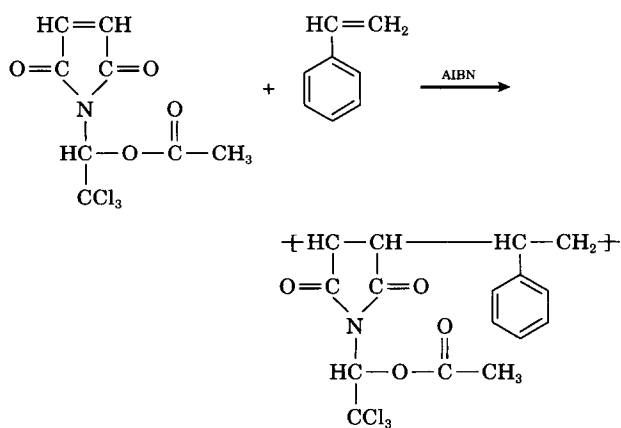


Figure 3 IR spectra of (a) copolymer [styrene-co-*N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide], (b) *N*-(1-acetoxy-2,2,2-trichloroethyl)maleimide, and (c) polystyrene.



The yields of imidization and copolymerization reactions are 65 and 91%, respectively. They seem to be large enough for technological purposes.

Thermal Stability of Copolymer StMI

To examine the thermal stability of copolymer StMI and compare it to the polystyrene, thermogravimetric analysis (TGA) measurements were made. The beginning of melting of the copolymer was observed by using Boethius apparatus at about 215°C. The TG and DTG curves (Fig. 4) show that the

decomposition of the copolymer begins at 275°C, and it occurs in two steps. Almost 100% mass loss is observed at 500°C. The temperature of decomposition of the copolymer is a few grades higher than the temperature of polystyrene. The measurement of fire resistance of the copolymer made by the test for flammability of plastics materials UL 94 shows that the copolymer is self-extinguishing (in the class 94V-1).

Conclusion

N-(1-hydroxy-2,2,2-trichloroethyl) maleamide undergoes imidization and acetylation in acetic anhydride. The product of the reaction, *N*-(1-acetoxy-2,2,2-trichloroethyl) maleimide, copolymerizes with styrene. In comparison with polystyrene thermal stability of the copolymer is almost the same, but fire resistance of the copolymer is essentially improved. The copolymer is self-extinguishing.

The results of the work proves that chloral substituent at a nitrogen atom in monomaleamide makes the imide ring closure possible. It means that imidization of *N*-(1-hydroxy-2,2,2-trichloroethyl) maleamide may be also carried in other ways, e.g., thermally or using another dehydrating agents. Thus it is possible to obtain *N*-(1-hydroxy-2,2,2-trichloroethyl) maleimide and a big variety of new monomers or comonomers by modification of it, e.g., grafting, crosslinking, esterification, etc. *N*-(1-acetoxy-2,2,2-trichloroethyl) maleimide may be modified (e.g., by hydrolysis or transesterification) as well.

The copolymers based on these monomers may be assumed to have good fire resistance.

Table II Calculated and Found Compositions of MI and StMI

Element	Elemental Analysis (% wt)			
	MI		StMI	
	Calculated	Found	Calculated	Found
C	33.5	34.0	49.2	48.9
H	2.1	2.5	3.6	4.0
N	4.9	4.7	3.6	4.2
O	22.3	23.1	16.4	17.0
Cl	37.2	35.7	27.3	25.9

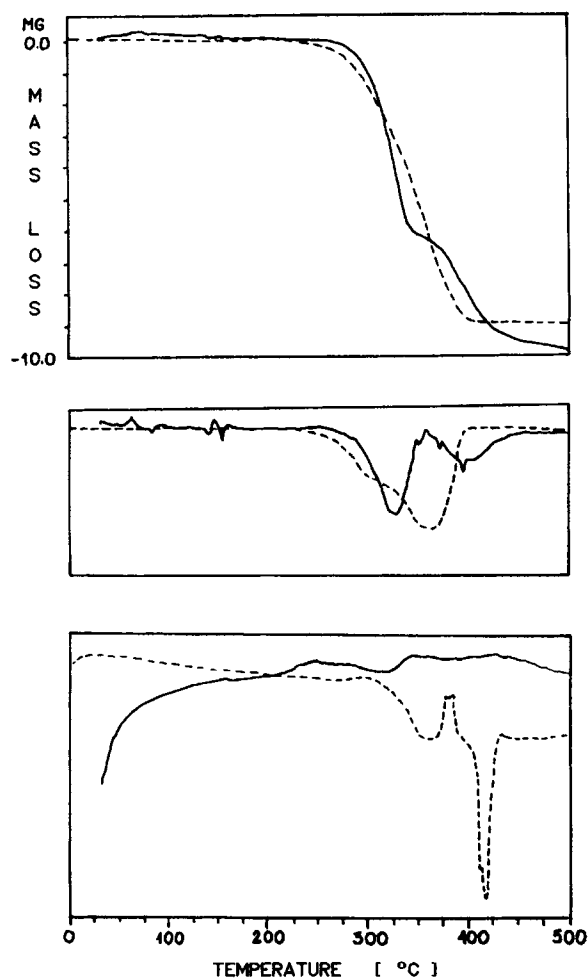


Figure 4 TG, DTG and DTA curves of (-----) polystyrene and (—) StMI.

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