

Copolymerization of *N*-Phenyl Maleimide and γ -Methacryloxypropyl Trimethoxysilane

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SYNOPSIS

Copolymerisation of *N*-phenyl maleimide (NPM) and γ -methacryloxypropyl trimethoxysilane (MTS) in dioxan solution using benzoyl peroxide as an initiator is described. The rate of copolymerisation depended on the mole fraction of NPM in the initial feed and decreased with an increase in NPM content. Copolymers having a mole fraction of NPM varying from 0.29 to 0.55 exhibited similar thermal behaviour in terms of initial decomposition temperature or temperature of maximum rate of weight loss. However, char yield at 600°C depended on NPM content, showing a tendency to increase with the increase in NPM content. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Copolymerisation behaviour of 1,2-disubstituted vinyl monomers such as maleimide, *N*-phenyl maleimide (NPM), and *N*-(4-substituted phenyl) maleimide with several vinyl monomers has been reported in the literature.¹⁻⁵ However, there have been no studies on copolymerisation of *N*-phenyl maleimide and unsaturated silanes. Such studies can provide useful information about the nature of interphase in glass-fibre reinforced bismaleimide resin composites. Copolymerisation of the maleimido group with unsaturated silanes (applied as a finish on glass fibres) may yield an interphase that may be distinct from the bulk of bismaleimide resin. Only a few studies dealing with the reaction of functional silanes with matrix resins have appeared in literature.^{6,7}

The reaction of amino silane with bismaleimide resin has been described recently.⁸ Copolymerisation of vinyl silanes with vinyl esters, vinyl chloride, alkyl esters, maleates, and vinyl pyrrolidone and of methacrylate functional silanes with alkyl methacrylates/styrene have also been reported.⁹⁻¹⁴

The present studies were undertaken to study the *in situ* reaction of bismaleimide resin with unsatu-

rated silanes. The problem with bismaleimide resins is the formation of a cross-linked product that is difficult to characterise. Therefore, NPM, which is a model compound for studying the behaviour of bismaleimide resins, was selected. The copolymerisation of NPM and γ -methacryloxypropyl trimethoxy silane (MTS) is described in this paper. Several copolymer samples were prepared by changing the molar ratio of two monomers in the initial feed. The rate of copolymerisation and the thermal behaviour of copolymers were also investigated.

EXPERIMENTAL

Materials

N-phenyl maleimide was prepared as described earlier.⁵ Dioxan (E. Merck)[#] was distilled before use. γ -Methacryloxypropyl trimethoxysilane (Kenrich Petrochem. Inc.) was used as received. Benzoyl peroxide (Loba Chemie) was recrystallised from chloroform.

[#] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

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Copolymerisation of NPM and MTS

In a flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet tube, known quantities of NPM and MTS were introduced. Three sets of monomer feeds, having mole fractions of NPM as 0.3, 0.5, and 0.7 were used. Dioxan was then added to yield an ~ 20% (w/v) solution. Nitrogen gas was passed through the solution, and the temperature was raised to $80 \pm 1^\circ\text{C}$. Benzoyl peroxide (1% w/w) was introduced into the flask and the reaction was carried out for a desired interval of time. The copolymer solution was then poured into petroleum ether to stop the reaction. The precipitated copolymers were filtered and dried at 60°C in a vacuum oven.

Characterisation

The structural characterisation of copolymers was obtained by recording IR spectra in KBr pellets using a Biorad Digilab FTS-40 FTIR spectrophotometer. The copolymer composition was determined by C,H,N analysis using a Perkin Elmer 240C elemental analyser. For silicon estimation, the polymer sample was charred at 200°C by adding a few drops of 1 : 1 HNO_3 : H_2SO_4 solution. Char was then heated in a furnace at 800°C for 2 h and the silicon dioxide thus obtained was weighed on cooling. The copolymer composition was then calculated. Thermal stability of copolymers in a nitrogen atmosphere (flow rate $60 \text{ cm}^3/\text{min}$) was assessed using a DuPont 1090

Table I Copolymerization of NPM and MTS

| Mole Fraction of NPM in Feed | Sample Designation | Duration of Reaction (min) | Conversion (%) |
|------------------------------|--------------------|----------------------------|----------------|
| 0.3 | 3M1 | 30 | 2.80 |
| | 3M2 | 60 | 13.10 |
| | 3M3 | 75 | 27.77 |
| | 3M4 | 90 | 39.20 |
| | 3M5 | 120 | 70.28 |
| 0.5 | 5M1 | 30 | 1.86 |
| | 5M2 | 45 | 4.62 |
| | 5M3 | 60 | 13.73 |
| | 5M4 | 90 | 16.22 |
| | 5M5 | 120 | 29.71 |
| 0.7 | 7M1 | 120 | 0.65 |
| | 7M2 | 150 | 0.64 |
| | 7M3 | 180 | 14.14 |
| | 7M4 | 210 | 17.35 |
| | 7M5 | 240 | 25.90 |

Table II Elemental Composition of Copolymers

| Sample Designation | Elemental Composition (%) | | | | Mole Fraction of NPM in Copolymer ^a |
|--------------------|---------------------------|-----|-----|------|--|
| | C | H | N | Si | |
| 3M2 | 48.3 | 6.6 | 1.8 | — | (0.29) |
| 3M3 | 48.1 | 6.5 | 2.0 | 8.70 | 0.30 (0.32) |
| 3M4 | 44.5 | 6.5 | 2.0 | 8.80 | 0.29 (0.32) |
| 3M5 | 49.1 | 6.7 | 2.1 | 7.90 | 0.38 (0.33) |
| 5M2 | 48.9 | 5.9 | 3.1 | — | (0.47) |
| 5M3 | 49.8 | 6.0 | 3.0 | 7.10 | 0.46 (0.46) |
| 5M4 | 49.7 | 6.1 | 2.8 | 7.30 | 0.44 (0.43) |
| 5M5 | 51.8 | 6.5 | 2.9 | 6.90 | 0.48 (0.45) |
| 7M3 | — | — | — | 4.98 | 0.66 |
| 7M4 | — | — | — | 5.60 | 0.59 |
| 7M5 | — | — | — | 6.06 | 0.55 |

^a Mole fraction of NPM in copolymers was determined by Si estimation or by nitrogen estimation. The values in parenthesis indicate copolymer composition calculated on the basis of nitrogen estimation.

thermal analyser having a 951 TG module. A sample size of $11 \pm 2 \text{ mg}$ and heating rate of $10^\circ\text{C}/\text{min}$ was used.

RESULTS AND DISCUSSION

Copolymerisation was carried out by using three different mole fractions of NPM in the initial feed (i.e., 0.3, 0.5, and 0.7). The rate of copolymerisation and copolymer composition for different monomer feed was determined. The rate of copolymerisation was determined by carrying out the reaction for different intervals of time while keeping the concentration of reactant and initiator constant. The extent of reaction was estimated gravimetrically by weighing the copolymer formed. The results are summarised in Table I. An induction period ranging from 30 min to more than 2 h was observed. An increase of NPM mole fraction from 0.3 to 0.7 considerably enhanced the induction time.

The rates of polymerisation (percent conversion per unit time) were obtained from the steady portion of percent conversion vs. time plots and were found to decrease from 0.9629 to 0.2804% per minute with an increase in NPM content in the initial monomer feed. On the basis of induction time and rate of

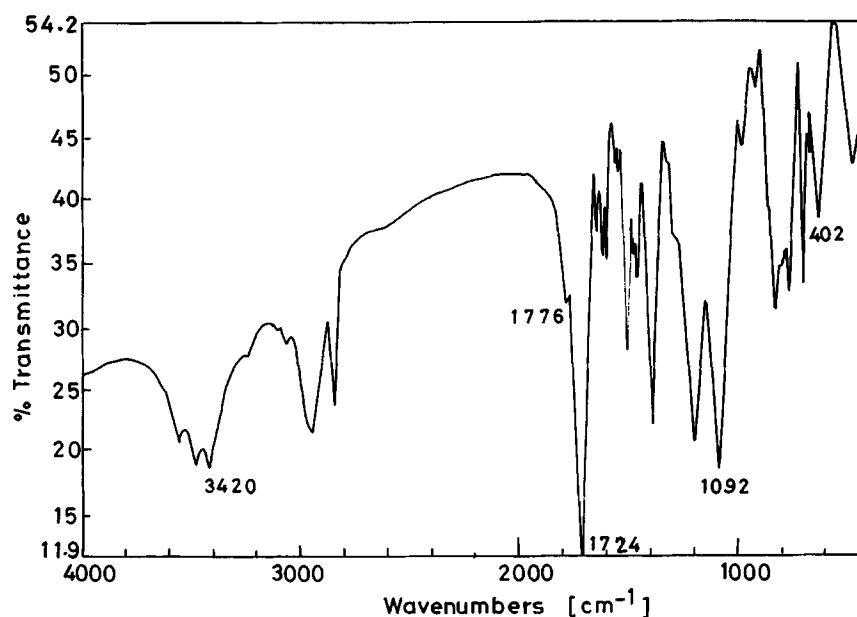


Figure 1 IR spectrum of 7M5.

polymerisation, it was concluded that cross-propagation reactions as well as initiation is reduced in the presence of NPM.

The results of elemental analysis (C,H,N,Si) of these copolymers are summarised in Table II. The NPM content in copolymers could be estimated from the nitrogen content. Alternatively, the estimation of Si gives information about the MTS mole fraction, from which the NPM content could be computed.

The copolymer composition as determined by these two methods is given in Table II. Similar copolymer compositions were observed on the basis of nitrogen or silicon content of the polymers. For a given monomer feed, the copolymer composition was almost constant irrespective of percent conversion in the steady state of copolymerisation (i.e., after the induction period).

The copolymers were characterised by IR spectroscopy. The characteristic peaks of the imide group and alkoxy silane were observed at 1776, 1724 ($\nu_{C=O}$ of imide), 1092 (Si—O—C bending) and 402 cm^{-1} (Si—O—C antisymmetric bend) (Fig. 1).

The intrinsic viscosities of the copolymers could not be determined because copolymers were partially insoluble in chloroform.

Endothermic transitions were observed in differential scanning calorimeter (DSC) scans of sample 7M1, 7M2, 7M3, 5M1, 5M2, and 5M3. In these samples, the concentration of NPM in initial feed was high and the percent conversion was low. It is quite likely that some unreacted NPM as well as low molecular weight product may be present as impurities.

In most of the copolymer samples mentioned above, the endotherm was above 150°C except in 7M1 and 7M2 where a broad endotherm was present in the temperature range 71–95°C, and another relatively sharp endotherm was above 180°C with endothermic peak temperature of 182° (7M1) or 187°C (7M2). Since the melting point of NPM is 88.9°C, the tran-

Table III Thermal Behaviour of Copolymers

| Sample Designation | T_i | T_{max} | T_f | Y_c (at 600°C) |
|--------------------|-------|-----------|-------------|---------------------|
| 3M1 | 361 | 391 | 422 (84.88) | 15 |
| 3M2 | 367 | 399 | 435 (83.44) | 16 |
| 3M3 | 368 | 398 | 432 (84.48) | 15 |
| 3M4 | 366 | 400 | 438 (82.93) | 17 |
| 3M5 | 370 | 402 | 439 (85.58) | 15 |
| 5M1 | 160 | 177.3 | 220 (15.67) | 28 |
| | 379 | 405 | 449 (59.39) | |
| 5M2 | 148 | 165.9 | 200 (8.52) | 26 |
| | 356 | 389 | 432 (65.97) | |
| 5M3 | 140 | 161.2 | 190 (4.84) | 26 |
| | 368 | 408 | 455 (71.19) | |
| 5M4 | 362 | 392 | 432 (81.39) | 19 |
| 5M5 | 363 | 392 | 456 (77.42) | 21 |
| 7M3 | 143 | 183 | 220 (6.89) | 30 |
| | 369 | 414 | 437 (59.47) | |
| 7M4 | 147 | 190 | 230 (7.20) | 23 |
| | 359 | 408 | 444 (78.59) | |
| 7M5 | 150 | 190 | 250 (5.42) | 23 |
| | 364 | 406 | 449 (72.35) | |

Figures in parenthesis indicate percentage weight loss.

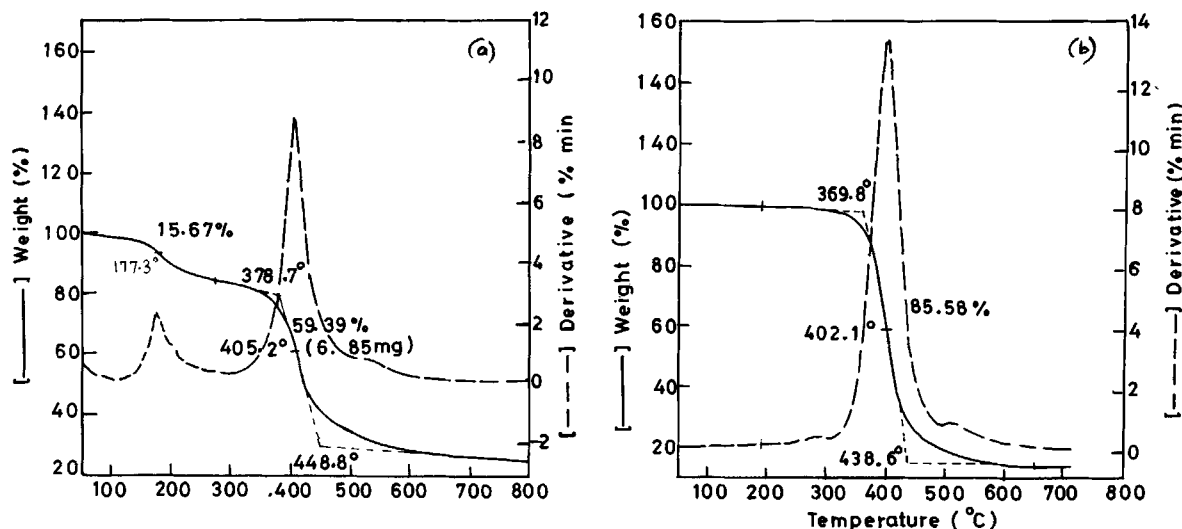


Figure 2 Thermogravimetric traces of (a) 5M1 and (b) 3M5.

sition at 71–95°C for 7M1 and 7M2 can be partially attributed to NPM. The high temperature endotherm may be caused by low molecular weight copolymers. Treatment of copolymers in boiling methanol resulted in the disappearance of this endotherm, which further lends support to the presence of oligomers. The weight loss observed by treatment with methanol was 3–7%.

The possibility of homopolymer formation during copolymerisation was studied by DSC. For this purpose, homopolymerisation of MTS and NPM was carried out separately in benzene for several hours at 78°C using benzoyl peroxide as an initiator. The polymers were recovered by precipitation. The homopolymer of MTS was heated for 0.5 h in aqueous methanol to cross link the polymer. In the DSC scans of MTS homopolymer, endothermic transitions were observed at -6° and 37°C while in cross-linked polymer these were at 8° , 68° , and 148°C . In NPM homopolymer no transition was observed up to 300°C (T_g of NPM is 248°C^1). Such endothermic transitions were not observed in copolymers, therefore, it can be concluded that homopolymer of MTS or NPM were not formed.

Thermal behaviour of these copolymers was investigated in a nitrogen atmosphere. From the T_g trace, initial decomposition temperature (T_i), final decomposition temperature (T_f) and percent char yield (Y_c) at 600°C were determined. From differential thermogravimetric (DTG) trace, the onset of degradation and the temperature of maximum rate of weight loss (T_{max}) was noted. These results are summarised in Table III.

A two-step decomposition was observed in all

these copolymer samples where the presence of oligomers was indicated by DSC and methanol solubility [Fig. 2(a)]. The weight loss in the temperature range of 150–200°C was very high ($44 \pm 3\%$) for 7M1 and 7M2 and 15% for 5M1. For other samples, it was below 8%. Major weight loss was observed above 300°C . Treatment of these samples with methanol changed the weight-loss pattern. In such samples only one step decomposition was observed above 350°C .

Thus, the copolymers of NPM and MTS obtained at low conversions from a monomer feed relatively rich in NPM leads to the formation of oligomers. As conversion is increased, these oligomers are converted to high molecular weight and a single step decomposition is observed [Fig. 2(b)]. This behaviour is contrary to the one observed in chain-growth polymerisation where high molecular weight product is expected to be formed from the very beginning, that is, even at very low conversion.

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