STUDIES ON TRIMETHOXY SILANE MODIFIED POLYMERS

By

ANIL KUMAR TOMAR

Centre for Materials Science & Technology

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DEDICATED
TO
MY
PARENTS

CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON TRIMETHOXY SILANE MODIFIED POLYMERS" being submitted by Mr. Anil Kumar Tomar to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Polymer Chemistry, is a record of bonafide research work carried by him. Mr. Anil Kumar Tomar has worked under our guidance and supervision and has fulfilled the requirement for the submission of this thesis, which to our knowledge, has requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

R C Anand

(R.C. ANAND)
Assistant Professor
Department of Chemistry
Indian Institute of Technology
New Delhi - 110016

I. K. Varma

(I.K. VARMA)
Professor of Polymer Science &
Head, Centre for Materials
Science & Technology
Indian Institute of Technology
New Delhi - 110016

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ABSTRACT

In the present studies the objective was to develop crosslinked polyalkyl methacrylate by introducing low mole fraction of γ-methacryloxy propyl trimethoxy silane in the backbone. Thus instead of producing thermosetting polyalkyl methacrylates, one can produce crosslinked products by exposure to moisture. Systematic studies are necessary to evaluate the effect of comonomer concentration on moisture induced crosslinking. The effect of substituents in the comonomers on crosslinking also needs investigation. Therefore, in the present studies low mole fractions of γ-methacryloxy propyl trimethoxy silane (MTS) were polymerised in presence of methyl methacrylate, ethyl methacrylate and butyl methacrylate. Higher concentration of MTS were not used because by increasing the crosslinked density, the brittleness of material would increase thereby reducing the impact resistance of the product. The aim was to optimise the mole fraction of MTS in the copolymers which is necessary to bring about desired crosslinking. Since MTS is not indigeneously manufactured, therefore, one of the objective was also to optimise the condition for the preparation of this monomer.

Yet another objective of the present studies was to evaluate the effect of silane coupling agents on curing characteristics and thermal behaviour of bismaleimide resin, which are thermosetting resins and are used as binders for

glass fibres. In order to compatibilise these matrix resins with glass fibres appropriate coupling agents are used such as γ-aminopropyl trimethoxy silane.

Conditions for the synthesis of MTS were optimised. It was prepared by using a three step process i.e. (a) synthesis of allyl methacrylate (b) its reaction with γ-methacryloxy propyl trichloro silane and (c) methanolysis of the γ-methacryloxy propyl trichloro silane to yield MTS. An overall yield of 51% was obtained using platinum tetrachloride and mesityl oxide as catalyst. It was found that (a) allyl methacrylate in approximately 85% yield could be obtained by using 1:1.21:1.13 molar ratio of methacrylic acid:thionyl chloride:allyl alcohol. By using $Pt(MeS)_2\ Cl_2$ complete catalyst maximum yield upto 63% could be obtained step (b) under mild reaction conditions. The duration of reaction was also reduced significantly. The methanolysis of γ-methacryloxy propyl trichloro silane to MTS was fairly quantitative (90-95% yield) and fast reaction (step c).

The free radical solution copolymerisation of MTS with MMA, EMA and BMA was carried out in nitrogen atmosphere in benzene and toluene (20% w/w) using 1% benzoyl peroxide as an initiator. The mole fraction of MTS in the initial feed was varied from 0.0099 - 0.0909. Several copolymer samples could thus be obtained and were separated from the solution by precipitation with petroleum ether ($40-60^{\circ}$) or methanol.

Precipitated copolymers were then filtered and dried at 50-60°C for 12h. Effect of temperature on copolymer composition was studied by carrying out the copolymerisation at 70° & 78°C (benzene solution), 80° and 100°C (toluene solution). The effect of time on percentage conversion was evaluated by carrying out the copolymerisation from 15 min to 105 min. It was observed that percentage conversion increased with the increase of temperature from 80° to 100°C and also with the increase of duration of reaction. The maximum percentage conversion at 80°C in most cases was around 40% which increased to about 80% at 100°C. The percentage conversion was almost independent of molar ratios of monomers in the initial feed.

Copolymers having low silicon content corresponding to 1 MTS unit per 63 MMA/405 EMA/60 BMA units or high silicon content corresponding to 1 MTS unit per 5 MMA/9 EMA/9 BMA units could be obtained by changing the mole fraction of MTS from 0.0099 to 0.0909 in initial feed.

The characteristic peaks of alkyl acrylates and MTS were observed in the ir spectra of copolymers at 1740 cm^{-1} (C=O), 1458-1450 cm^{-1} (CH_2-bending), 1088-1080 cm^{-1} (Si-O-C bending), 486 cm^{-1} (Si-O-C assymetric bend). The peak at 1088 cm^{-1} increased in intensity as the MTS content increased in the feed.

In the pmr spectra the characteristic proton resonance signals observed in MMA:MTS copolymers were at 3.6 (due to $-COOCH_3$ of MMA, OCH_3 and OCH_2 of MTS), 1.89 ppm (due to $-CH_2$ protons), 1.0 ppm (due to $-CH_3$ of MMA & MTS) and 0.8 ppm (due to CH_2-Si protons). Structural assignment of EMA:MTS and BMA:MTS copolymers was done by using pmr technique. The proton signal due to methoxy group of silane (3.6 ppm) was used to find out the relative concentration of MTS in these copolymers.

The intrinsic viscosity of copolymers of MTS with MMA, EMA and BMA was around 0.42 ± 0.05 dl/g, 0.10-0.25 dl/g and 0.09-0.25 d /g respectively. Copolymers containing high MTS content were partially insoluble in chloroform or DMF hence their intrinsic viscosity could not be determined. The of copolymers prepared at 78-80°C.

The hydrolysis of MS, ES & BS copolymers in the presence of water at 85°C was carried out for different time intervals. In MMA:MTS copolymers with higher MTS content, more than 96% gel formation was observed after 30 min of hydrolysis. Increase in MTS in MS copolymers resulted in an increase in gel formation. The gel formation increased significantly (6.7 to 86.6%) as the mole fraction of MTS increased in the copolymer from 0.0131 to 0.0539. Further increase in MTS in copolymer did not affect the % gel formation significantly. For example a three fold increase in mole fraction of MTS (i.e. from 0.0539 to 0.1508) resulted only in a 7% increase in gel formation. Thus an optimum mole fraction of MTS in copolymer is sufficient to bring about the maximum extent of crosslinking.

Copolymers having low MTS in the backbone showed a dependence of crosslinking on duration of hydrolysis. A two to five fold increase in gel formation was observed by increasing the duration of hydrolytic condensation from 1h to 24h in copolymer having low mole fraction of MTS (i.e. 0.0131-0.0292). No change in % gel formation with time was observed in copolymer samples having high mole fraction of MTS in the backbone.

Hydrolytic condensation was a relatively slow process in ES & BS copolymer series. For example MS^{b}_{59} which contained 0.0539 moles of MTS, 96% gel formation was observed whereas in ES^{b}_{612} having 0.0651 mole fraction of MTS, the % gel formed was only 59%. The solubility behaviour of crosslinked material obtained after treatment with water was also determined in $CHCl_3$. In both ES & BS copolymers, % gel formation was lower than that in MS copolymers. The lower rate of hydrolytic condensation in ES & BS copolymers can be attributed to the bulky alkyl group of methacrylates. Due to steric hindrance of these bulky substituents, condensation of silanol groups with each other may have been hindered thereby reducing the crosslinking reaction.

Two to three step degradation was observed in TG traces depending on the mole fraction of MTS in copolymer. In uncross-linked copolymers almost complete loss in weight occured at 400°C, 410°C and 425°C in copolymers of MTS with MMA, EMA and BMA respectively. The small residual weight above these temperatures depended on initial silicon content. The T_{max} values for MTS/MMA and MTS/EMA copolymers were at 298 ± 3°C and 380 ± 3°C and for MTS/BMA copolymers were at 300 ± 2°C and 350 ± 3°C. Hydrolysis of copolymers containing low mole fraction of MTS only marginally affected the thermal behaviour. Copolymers prepared at high temperature and having lower $[\eta]$ values were found to be less stable thermally. This indicates the participation of end-groups in thermal degradation. At lower temperatures (150-250°C) the major products of decomposition of copolymers is MMA while at high temperature MTS formation takes place in larger quantities.

4,4'-bis(maleimidophenyl) methane was synthesized in the laboratory by reacting maleic anhydride (2.2 mole) with 4,4'-diaminodiphenyl methane (1 mole). The reaction was carried out at 55-60°C for 2h in DMF and the cyclization of the amic acid intermediate was done by treating with fused sodium acetate and acetic anhydride. The solution was then cooled and BM was precipitated by pouring the solution in excess of water. The precipitates were washed with sodium bicarbonate solution, distilled water, dried and recrystallised from chloroform after passing through silica gel column. The reaction of BM with ATS was carried out in methylethyl ketone (20% w/w). One mole of BM was dissolved in MEK and 0.01 to 0.30 mole of ATS was added and heated at 80°C for 90 min. The effect of time (30-105 min) on the adduct formation was also studied.

In ir traces the peak at 1080-1020 cm^{-1} ($>Si-O-C-$) increase in intensity as the mole fraction of ATS increased in these adducts. The bands at 1720 cm^{-1} and at 3480 cm^{-1} were assigned due to carbonyl stretching and -NH stretching vibrations respectively. The peak at 1550 cm^{-1} due to -NH bending was also present.

The structure of BM:ATS adducts was deduced by determining the ratio of aromatic proton to vinylic proton using pmr. The proton ratio thus obtained indicated lesser number of vinylic bonds than expected on the basis of molar ratio of BM & ATS taken in the initial feed. This observation indicates the addition of silanol hydroxy groups to maleimide double bonds by nucleophilic addition.

An exothermic transition representing curing reaction was observed in the temperature range of 150°C to 330°C. The temperature of onset of curing, maximum temperature of curing (T_{exo}) and final curing temperature decreased on increasing the mole fraction of ATS in the BM-ATS adduct. The area under the exotherm, which is a measure of heat of polymerisation, decreased from 264 J/g to 104 J/g as the mole fraction of ATS in adduct increased. The BM-ATS adducts having different concentration of ATS were cured at 180°C for 1h and then at 200°C for 1h. The extent of crosslinking was evaluated by solubility measurements in DMF.

The temperature of initial decomposition, the temperature of maximum rate of weight loss and final degradation temperature of the BM-ATS adducts decreased with the increase in concentration of ATS in the adduct. The % char yield at 800°C was in the range of 45-55%.

CONTENTS

Page No.

CHAPTER I LITERATURE SURVEY

CHAPTER II SYNTHESIS OF γ-METHACRYLOXY PROPYL TRIMETHOXY SILANE AND ITS COPOLYMERISATION WITH ALKYL METHACRYLATES

CHAPTER III CHARACTERIZATION OF COPOLYMERS

CHAPTER IV HYDROLYTIC CONDENSATION AND THERMAL BEHAVIOUR OF COPOLYMERS

CHAPTER V SYNTHESIS OF 4,4'-BIS(MALEIMIDOPHENYL) METHANE AND ITS ADDUCTS WITH γ-AMINO PROPYL TRIMETHOXY SILANE