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Synthesis and Studies of Properties of Crosslinkable Copolymers Based on Methyl Methacrylate

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ABSTRACT

Copolymers of methyl methacrylate(MMA) with polypropylene glycol diacrylate(PPGDA) and polypropylene glycol dimethacrylate(PPGDMA) have been synthesized. The characterization of synthesized copolymers are carried out using the techniques such as elemental analysis, Fourier Transform Infrared Spectroscopy(FTIR) and Differential Scanning Calorimetry(DSC). FTIR studies showed that double bond of MMA and crosslinker has reacted. During the reaction between MMA and PPGDA or PPGDMA double bond reacts on both ends and formed the crosslinked network structure. DSC studies showed that Glass Transition Temperature(T_g) for three copolymers are lower while for one copolymer it is slightly higher than that of polymethylene methacrylate(PMMA). Higher value of T_g suggests that crosslinking has increased in this copolymer while lower value of $T_g$indicates lower crosslinking level.

Keywords: Polymers, synthesized copolymers, Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy(FTIR)

INTRODUCTION

Copolymerization is one of the important technique adopted to achieve systematic changes in the properties of commercially important polymers[1]. Acrylates and methacrylates are highly versatile building blocks that readily polymerize or copolymerize with variety of other monomers[2]. Because of clarity, toughness,light resistance,stability and chemical inertness, the acrylic ester dispersion polymers are extensively used in coating. These are used as prime paint vehicle in all types of paint formulations such as interior, exterior, primer, basecoat and topcoats. The acrylic emulsions are also used for industrial finishing of surfaces of wood, metal etc.

Crosslinked copolymers of MMA have been widely studied for their potential in various fields. Water soluble copolymers of PMMA grafted with polyethylene glycol find increasingly importance as hydrogels in the biomedical field[3]. Copolymers of MMA and butyl acrylate with N-methyloacrylamide as a crosslinking agent is used in textile coatings[4]. Copolymerization of diacrylates/dimethacrylates of various glycols and various allyl esters have been investigated by several workers[5-8].

Copolymers of MMA are widely used in coatings because of its film forming capacity which is due to better bond forming tendency with various substrates. Copolymers of MMA with different monomers such as butyl acrylate, 2-ethyl hexyl acrylate, hydroxyl ethyl methacrylate are extensively used for coatings on different substrates to improve the roughness, acid scratch and solvent resistance.

The present work deals with the synthesis of copolymers of MMA with PPGDA and PPGDMA and to analyze the copolymers obtained. Therefore, the characterization of synthesized copolymers are carried out using the following techniques:

1 Elemental Analysis of copolymers.
2 Fourier Transform Infrared Spectroscopy (FTIR) of synthesized copolymers.
3 Differential Scanning Calorimetry (DSC).

Table 1: Recipe Used For The Emulsion Polymerization

Sr. No.	Materials	Amount
1	Water	65 ml
2.	Monomer	10 g
3.	Crosslinker	(0-40 wt %)
4.	Sodium Lauryl Sulphate	9×10^{-3} – $3.18\text{x}10^{-2}$ mol/L H_2O
5.	Potassium Persulphate	$4.5\text{x}10^{-3}$ – $12.5\text{x}10^{-3}$ mol/L H_2O

EXPERIMENTAL

Chemicals

MMA used was obtained by Fluka. PPGDA4, PPGDA12, PPGDMA4 and PPGDMA12 were purchased from S. D. Fine Chemicals Ltd., Mumbai.

Polymerization

The copolymers of MMA with various crosslinkers were synthesized by emulsion polymerization technique. Polymerization was conducted in a three neck round bottom flask fitted with a stirrer in the center, a nitrogen inlet on one side and a condenser on the other side using a stirred oil bath set at a temperature of 50^{0}C. for polymerization de-ionized water was taken in a flask and a part of emulsifier was added to it. When the emulsifier gets dissolved the rest of the emulsifier was added and dissolved. The copolymer which includes MMA and

Table 2: I R Peaks of Various Types of Bonds

Sr. No.	Bond and Type of Compound	Frequency Region (cm^{-1})	Frequency(cm^{-1}) PMMA	MMA-PPGDA4	MMA-PPGDMA4	MMA-PPGDA12	MMA-PPGDMA12
1.	C-O bond in esters, alcohols, ethers,carboxylic acids	1080-1300	1150.5	1148.8	1101	1100	1109.6
2.	>C=O in aldehydes,ketones, esters, carboxylic acids	1690-1750	1735	1733.7	1726.6	1735.7	1734.0
3.	C-C bond in alkanes	600-1500	1352.8	987.8	919.1	936.5	901.0
4.	C-H bond in alkanes	2850-2960	2925.9	2952.4	2928.3	2929.5	2928.6
5.	C=C bond in alkenes	1620-1680	1660	Low intensity	Low intensity	Low intensity	Low intensity

PPGDA4 was added drop by drop with continuous stirring for 15 minutes in three neck flask. At last, initiator was added to initiate the reaction. Similarly the addition of copolymer having MMA and other monomers was done.

Elemental Analysis

The presence of oxygen in the copolymer was confirmed by the presence of carbonyl group and ester group in the copolymer by 2,4-dinitrophenyl hydrazine test for carbonyl group and ester test for ester group.

FTIR Studies

FTIR studies were obtained by using Shimadzu 8201 PC FTIR Spectrometer from CDRI, Lucknow.

DSC STUDIES

DSC studies were obtained from CIPET, Lucknow.

RESULTS AND DISCUSSIONS

Elemental Analysis

Elemental analysis confirmed that only carbon, hydrogen and oxygen are present in the copolymers and no extra elements such as N,P,S and halogens are present. The presence of oxygen as >C=O and –COOR groups were also confirmed by the test for carbonyl and ester groups .

FTIR Studies

Four copolymers of MMA with different crosslinkers (PPGDA4, PPGDMA4, PPGDA12, PPGDMA12) were prepared and analyzed by FTIR studies in the frequency range 4000 – 400 cm^{-1}.

Table 3: Glass Transition Temperature (T_g) For Various Copolymers (Heating Rate 5^0C Per Minute)

Sr. No.	Copolymer	$T_g(^0C)$
1.	PMMA	105
2.	MMA-PPGDA4	79
3.	MMA-PPGDMA4	106.1
4.	MMA-PPGDA12	54
5.	MMA-PPGDMA12	57

In the FTIR spectra of copolymers, the absorbance appearing in the range 1726 -1736 cm^{-1} are due to >C=O linkages. The absorbance at 1100 – 1148 cm^{-1} can be attributed to –C-O-C- linkages.

The C –C bond in alkanes ranges between 600 -1500 cm^{-1}. The copolymers showed a sharp peak at 919.1cm^{-1} for MMA-PPGDMA4, 987.8 cm^{-1} for MMA-PPGDA4, 901.0 cm^{-1} for MMA-PPGDMA12 and at 936.5 cm^{-1} for MMA-PPGDA12.

C=C bond is present in PMMA and ranges between 1620 -1680 cm^{-1} found to be absent in the synthesized copolymers. It showed that double bond of MMA and crosslinker has reacted. During the reaction between MMA and PPGDA or PPGDMA, double bond reacts on both ends and formed crosslinked network structure. For the two copolymers MMA-PPGDMA4 and MMA-PPGDMA12 a high intensity peak is observed at 2928.3 cm^{-1} and 2928.6 cm^{-1} respectively, which is due to the presence of C-H bond of methyl group which are higher in number in MMA-PPGDMA12 in comparison to two copolymers MMA- PPGDA4 and MMA- PPGDA12.

On comparing the molecular weight of diacrylate and dimethylacrylates of copolymers, intensity of >C=O and C-O-C linkages increases, because of the presence of number of such groups.

Differential Scanning Calorimetry (DSC) Studies

DSC of PMMA shows that Glass Transition Temperature (T_g) is 105^0C [9] while for copolymer of MMA with PPGDA4 T_g is79^0C, for copolymer of MMA with PPGDMA4 T_g is 106.1^0C, for copolymer of MMA withPPGDA12 T_g is 54^0C and for copolymer ofMMAwith PPGDMA12 T_g is 57^0C.

The values of T_g for three copolymers (MMA – PPGDA4, MMA –PPGDA12 and MMA –PPGDMA12) are lower while for one copolymer (MMA –PPGDMA4) it is slightly higher than that of PMMA.

Higher value of T_g for MMA –PPGDMA4 than PMMA suggests that crosslinking has increased in this copolymer. On the other hand lower value of T_g for MMA –PPGDA4, MMA –PPGDA12 and MMA –PPGDMA12 than that of PMMA indicates lower crosslinking level. Hence MMA –PPGDMA4 which is a high T_g polymer provides a good blocking resistance and surface hardness to the films while MMA –PPGDA4, MMA –PPGDA12 and MMA –PPGDMA12 which are of low T_g polymers are responsible for good film elasticity, a sufficient film building without solvent and a high film gloss.

CONCLUSIONS

1. As no extra elements such as nitrogen, phosphorous, sulphur and halogens are present in any of the copolymers and the presence of oxygen as >C=O group and -COOR group confirmed that all copolymers under investigation have crosslinked through carbonyl and ester group.
2. The FTIR spectra also confirms the presence of carbonyl and ester groups in all the copolymers. C=C is present in PMMA crossponding to a peak at 1660 cm^{-1} while in other copolymers it is absent. This confirms that double bond of MMA and crosslinker has reacted.
3. The copolymers MMA –PPGDA4, MMA –PPGDA12 and MMA –PPGDMA12 which are having lower T_g value give good coating film on wood as a substrate to guarantee long service life.
4. The copolymer MMA –PPGDMA4 which is having higher value of T_g provides a good blocking resistance and surface hardness to the film. Therefore, it is found to be very useful in the ready paint film which should display a high blocking resistance and surface hardness.

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