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-methylocrylamide 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\textsuperscript{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).

**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°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>
<thead>
<tr>
<th>Sr. No.</th>
<th>Materials</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>65 ml</td>
</tr>
<tr>
<td>2</td>
<td>Monomer</td>
<td>10 g</td>
</tr>
<tr>
<td>3</td>
<td>Crosslinker</td>
<td>(0-40 wt %)</td>
</tr>
<tr>
<td>4</td>
<td>Sodium Lauryl Sulphate</td>
<td>9x10\textsuperscript{-3} – 3.18x10\textsuperscript{-2} mol/L H\textsubscript{2}O</td>
</tr>
<tr>
<td>5</td>
<td>Potassium Persulphate</td>
<td>4.5x10\textsuperscript{-3} – 12.5x10\textsuperscript{-3} mol/L H\textsubscript{2}O</td>
</tr>
</tbody>
</table>

**Table 1: Recipe Used For The Emulsion Polymerization**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bond and Type of Compound</th>
<th>Frequency Region (cm\textsuperscript{-1})</th>
<th>PMMA MMA-PPGDA4 MMA-PPGDMA4 MMA-PPGDA12 MMA-PPGDMA12</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C=O bond in esters, alcohols, ethers, carboxylic acids</td>
<td>1080-1300 1150.5</td>
<td>1148.8 1101 1100 1109.6</td>
</tr>
<tr>
<td>2</td>
<td>&gt;C=O in aldehydes, ketones, esters, carboxylic acids</td>
<td>1690-1750 1735</td>
<td>1733.7 1726.6 1735.7 1734.0</td>
</tr>
<tr>
<td>3</td>
<td>C-C bond in alkanes</td>
<td>600-1500 1352.8</td>
<td>987.8 919.1 936.5 901.0</td>
</tr>
<tr>
<td>4</td>
<td>C-H bond in alkanes</td>
<td>2850-2960 2925.9</td>
<td>2952.4 2928.3 2929.5 2928.6</td>
</tr>
<tr>
<td>5</td>
<td>C=C bond in alkenes</td>
<td>1620-1680 1660</td>
<td>Low intensity Low intensity Low intensity Low intensity</td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Sr. No.</th>
<th>Copolymer</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PMMA</td>
<td>105</td>
</tr>
<tr>
<td>2.</td>
<td>MMA–PPGDA4</td>
<td>79</td>
</tr>
<tr>
<td>3.</td>
<td>MMA–PPGDMA4</td>
<td>106.1</td>
</tr>
<tr>
<td>4.</td>
<td>MMA–PPGDA12</td>
<td>54</td>
</tr>
<tr>
<td>5.</td>
<td>MMA–PPGDMA12</td>
<td>57</td>
</tr>
</tbody>
</table>

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 919.1 cm\(^{-1}\) 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–PPGDMA12.

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°C\(^{[9]}\) while for copolymer of MMA with PPGDA4 \(T_g\) is 79°C, for copolymer of MMA with PPGDMA4 \(T_g\) is 106.1°C, for copolymer of MMA with PPGDA12 \(T_g\) is 54°C and for copolymer of MMA with PPGDMA12 \(T_g\) is 57°C.

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

Higher value of \(T_g\) for MMA – PPGDAMA4 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 corresponding 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.

**REFERENCES**


