Synthesis of Diacetone Acrylamide Monomer and the Film Properties of Its Copolymers

Nishant V. Tale and Ramanand N. Jagtap*

Department of Polymer and Surface Engineering, Institute of Chemical Technology, N.M. Parekh Marg, Mumbai-400019, India

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ABSTRACT

Diacetone acrylamide (DAAM) was derived from alkaline hydrolysis of 2-methyl-4-oxo-N-[(1Z)-1(sulphoxy)prop-2-ene-1-ylidene]pentan-2-aminium as a precursor which the latter was prepared by condensation of acrylonitrile and acetone in sulphuric acid. Diacetone acrylamide was characterized by $^1$H NMR, FTIR and mass spectrometry for structural conformation. The DAAM copolymer emulsions were prepared by a two-stage seed batch emulsion polymerization of methyl methacrylate, butyl acrylate and DAAM using ammonium persulphate as an initiator, sodium lauryl sulphate and nonyl phenol as emulsifiers. Diacetone acrylamide was used as a functional monomer. Further, the DAAM copolymer emulsions were characterized and studied as a function of DAAM concentration by laser light scattering, viscometry and differential scanning calorimetry. The results have shown that with increased concentration of DAAM in the emulsions there are increases in particle size, particle size distribution and viscosity of the emulsions, whereas the glass transition temperature ($T_g$) of DAAM emulsions is reduced. These emulsions comprising different concentrations of DAAM were cross-linked with 1,3-diaminopropane and were characterized by FTIR. The cross-linking reaction was carried out at ambient temperature resulting in formation of one-component thermoset acrylic emulsions. These emulsions which were used as coatings were evaluated for mechanical and chemical resistance properties. The results obtained showed that the coating comprised of 4 wt% of DAAM in copolymer emulsion exhibited improved chemical resistance and mechanical properties.

INTRODUCTION

Growing awareness and environmental legislations are imposing restrictions on the emission of volatile organic compounds (VOCs). These restrictions have forced coating manufacturer to formulate coatings comprised of low or zero content of VOCs. Emulsion polymerization is an important polymerization technique, as it yields high molecular weight polymers with low viscosity. Moreover, polymers can be tailor-made in order to exhibit desired composition and morphology [1-4].

Diacetone acrylamide (DAAM) is a vinyl functional monomer having good solubility and reactivity ratio with most of the comonomers and is capable of forming polymers and copolymers with exceptional ease [5,6]. The carbonyl groups of DAAM can readily cross-link with primary amines and form imines,

Key Words:
diacetone acrylamide; thermoset; seed batch emulsion copolymerization; 1,3-diaminopropane.

(*) To whom correspondence to be addressed. E-mail: rn.jagtap@ictmumbai.edu.in
whereas with secondary amines give enamines with elimination of water molecule [7,8]. The most striking features of this cross-link reaction is that it proceeds rapidly at ambient temperature, therefore it is environmentally friendly and non-hazardous, which makes it useful in a wide variety of applications like architectural coatings [9], wood coatings [10], water repellent coatings [11], inks [12,13] and adhesives [14-16]. Thus, it has been emphasized in the development of a one-component thermoset emulsion system curable at ambient temperature [17,18].

In some reported works [19-21], adipic acid dihydrazide (ADH) was comprehensively utilized as a cross-linker whereas in this contest, we used 1,3-diaminopropane as a cross-linker instead, because of some limitations with ADH properties, i.e., poor solubility in water (5 g/100 mL) which coagulates the emulsion when added directly and it is susceptible to alkaline and acid hydrolysis due to the presence of two amide linkages. Based on literature, DAAM was prepared from acetone, acrylonitrile and sulphuric acid by Ritter reaction [22-25].

In the present investigation, re-examination and modification have been applied on the reaction system of acetone-acrylonitrile-sulphuric acid. We report the formation of a water soluble intermediate, 2-methyl-4-oxo-\(N\)-(1Z)-1(sulphoxy)prop-2-en-1-ylidene)pentan-2-aminium (compound 3 in Scheme I). The obtained crystals were dissolved in 1/1(v/v) water/toluene mixture, and on standing the organic and aqueous layers separated. The monomer was extracted several times with toluene to form an aqueous layer. By collecting the organic layers and concentrating them under vacuum at 50-55°C and cooling them at 0°C, crystals of diacetone acrylamide (compound 4 in Scheme I) were obtained. The progress of reaction was monitored by TLC. Yield and melting point were

**EXPERIMENTAL**

**Material**

Acrylonitriles, methyl methacrylate (MMA), butyl acrylate (BA) were purified by treating with 10% of NaOH solution followed by washing with water to remove inhibitor and were dried over sodium sulphate. Acetones, sulphuric acid, ammonium persulphate, 1,3-diaminopropane of analytical grade were purchased from S.D. Fine Chem. Ltd. Co, (India). Nonylphenol 10 (NP 10), sodium lauryl sulphate (SLS) were used as emulsifiers, toluene, petroleum ether, sodium hydroxide, sodium bicarbonate were procured from Thomas Baker (India). De-ionized water was used throughout the experiment.

**Synthesis of Diacetone Acrylamide**

A mixture of 1 mol of acrylonitrile (compound 1 in Scheme I) and 2 mol of acetone (compound 2 in Scheme I) were added dropwise in to 1.2 mol of sulphuric acid 96% under constant stirring at 0°C over a period of 2 h, after the complete addition, the reaction mixture was heated at 45°C for 4 h. On completion of digestion, the reaction mixture was cooled to 0°C and diluted with acetone, resulting to the formation of crystals of 2-methyl-4-oxo-\(N\)-(1Z)-1(sulphoxy)prop-2-ene-1-ylidene)pentan-2-aminium (compound 3 in Scheme I). The obtained crystals were dissolved in 1/1(v/v) water/toluene mixture, and on standing the organic and aqueous layers separated. The monomer was extracted several times with toluene to form an aqueous layer. By collecting the organic layers and concentrating them under vacuum at 50-55°C and cooling them at 0°C, crystals of diacetone acrylamide (compound 4 in Scheme I) were obtained. The progress of reaction was monitored by TLC. Yield and melting point were
their respective values of 53% and 54-56°C.

**Synthesis of Copolymers of DAAM-MMA-BA Emulsion**

Sodium lauryl sulphate, NP10, and de-ionized water were added into a three-neck flask, equipped with a stirrer, a condenser, and thermometer. The entire assembly was placed in water bath connected to temperature controller maintained at 50°C, and the mixture was stirred at 100 rpm, followed by introducing a ratio of 1/4 pre-emulsion of monomers and initiator (APS 0.1 g in 1 mL water) into the three-neck flask, and raised the temperature of reaction mixture to 72°C and maintained for 20 min. A slight blue colour appeared which indicated the formation of seed latex particles. Now, the remaining monomer pre-emulsion was fed into the three-neck flask over a period of 3.5 h. The remaining initiator was divided into several equal portions and added to vessel at specific time intervals during monomer feeding, and in the mean time a buffer solution (NaHCO₃ solution) was also added at specific intervals. Once feeding was completed, the temperature was raised to 80°C for another 15 min. Finally the latex was cooled and filtered. The recipe of seed batch emulsion polymerization is summarized in Table 1.

**Table 1. The recipe of seed batch emulsion polymerization of DAAM-MMA-BA.**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Seed</th>
<th>Second stage weight (g)</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>8.25</td>
<td>11.85</td>
<td>11.85</td>
<td>11.85</td>
<td>11.85</td>
<td>11.85</td>
</tr>
<tr>
<td>MMA</td>
<td>4.25</td>
<td>23.85</td>
<td>24.85</td>
<td>25.85</td>
<td>26.85</td>
<td></td>
</tr>
<tr>
<td>DAAM</td>
<td>0.00</td>
<td>0.914</td>
<td>0.685</td>
<td>0.457</td>
<td>0.228</td>
<td></td>
</tr>
<tr>
<td>SLS</td>
<td>0.85</td>
<td>0.850</td>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>NP-10</td>
<td>0.55</td>
<td>0.550</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>APS</td>
<td>0.25</td>
<td>0.250</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.10</td>
<td>0.100</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>DI</td>
<td>27.0</td>
<td>27.00</td>
<td>27.0</td>
<td>27.00</td>
<td>27.00</td>
<td>27.00</td>
</tr>
</tbody>
</table>

![Scheme II. Synthesis of DAAM copolymer.](image-url)
Preparation of an Aqueous Cross-linker Solution
To make a 40% solution of 1,3-diaminopropane in the mixture of de-ionized water, propylene glycol monomethyl ether (PGME) and propylene glycol monopropyl ether (PGPE) at 37/3/20 wt% ratio were used. Propylene glycol monopropyl ether swelled the resin and enhanced the promoter penetration of the cross-linker. Phosphoric acid (3%) was added as a catalyst for cross-linking reaction.

The polymerization of DAAM, MMA, BA and cross-linking reaction of DAAM with 1,3-diaminopropane is shown in Schemes II and III.

Monomer Characterization
FTIR analyses (Shimadzu 8400s, Japan) of DAAM and emulsion were both recorded using ATR technique. $^1$H NMR spectrum of DAAM was recorded at 500 MHz using Bruker Biospin (Avance AV500WB, Germany) in CDCl$_3$. For GC-MS analysis, 10 ppm solution of DAAM was made in dichloromethane and recorded the chromatogram using Shimadzu (QP 2010, Japan).

Polymer Characterization
Particle size and particle size distribution of emulsion were measured using particle size analyzer based on laser scattering (Cilas, 1064, France). Differential scanning calorimetry (DSC) (Q100 V9.7 Build 291, USA) was performed at a rate of 10°C/min. A sample of 5-8 mg was put in an aluminium pan and used for thermal analysis in DSC instrument. Viscosity of the emulsion was measured using Brookfield viscometer (Antopar, GMBH, Austria)

Cross-linking Procedure for the Emulsion
Emulsions were coated on the treated M.S. panel by using a bar coater and then dried. The thickness of dried film was about 50 μm. The coated panels were dipped into a solution of 1,3-diaminopropane for 10 min at room temperature and were further washed with water and the remaining droplets on the surface wiped out with a filter paper. The weight of the swelled panel (A) was immediately recorded and the panel was dried for 10 min at 110°C to obtain the weight of dried panel (B). Swelling degree was calculated by following equation.

$$\text{Swelling} \% = \left( \frac{A - B}{C} \right) \times 100$$

where
- $A =$ weight of swelled panel
- $B =$ weight of the dried panel
- $C =$ weight of coating panel

Mechanical Testing on Coatings
Scrub resistance test was performed according to ASTM 2486-79 and the film results are given as number of cycles. Impact resistance was carried out on both sides of coated panels and analyzed in accordance to the standard ASTM D 2794. The results were categorized as fair (cracking), good (slight cracking) and best (no change).

Pencil hardness test was used to observe the hardness values of the films according to ASTM D 3363.
Figure 1. Relationships between the thickness of cross-linked layers of DAAM copolymer and dipping time in 1,3-diaminopropane solution at room temperature.

The scratch hardness was determined by an automatic scratch hardness tester as per ASTM D7027. For adhesion testing, cross-cut adhesion tape was used to assess the adhesion of film coated onto metallic substrate according to ASTM D 3359.

Alkali resistance of panels was evaluated for film whitening and blistering according to ASTM D 1647. Acid resistance of panels was evaluated for peeling and corrosion of coated part according to ASTM D 3260.

For water resistance testing, the coated panels were immersed in water and then, the panels were evaluated for colour change of coating, blistering, skinning according to ASTM D 870-02. Flexibility of the coated M.S. panel was determined by the conical mandrel according to ASTM D 522-93a, finally.

RESULTS AND DISCUSSION

Effect of Dipping Time on Degree of Cross-linking Reaction

Figure 1 shows correlations between dipping time and thickness of cross-linked layer of the emulsions at four different concentrations of DAAM.

The dry film thickness (DFT) of DAAM copolymers was 50±5 μm. These films were cured by dipping into 1,3-diaminopropane cross-linker for 10-30 min. It was observed that with increase in DAAM content and dipping time, the DFT value of the cured films was increased. Diacetone acrylamide as a polar monomer has high affinity towards water. Therefore, when DAAM content in the copolymer is increased from 1 wt% to 4 wt%, the swelling of the film is also increased leading to enhanced penetration of the 1,3-diaminopropane. This resulted into

Figure 2. FTIR Spectrum of 2-methyl-4-oxo-N-[(1Z)-1(sulfooxy) prop-2-ene-1-ylidene] pentan-2-aminium.
increased DFT value of the final cured film.

**FTIR Analysis of 2-Methyl-4-oxo-N-[(1Z)-1(sulphooxy)prop-2-ene-1-ylidene]pentan-2-aminium**

Figure 2 shows the peaks at 3169, 2818, 1720 and 1662 cm\(^{-1}\) assigned to \(-\text{NH str, aliphatic C-H str, C=O str, and amide str (C=O), respectively. The peak at 1613 cm}^{-1}\) is characteristic absorption band of intermediate C=N str. The peak at 1531 cm\(^{-1}\) is assigned to C=C, and those at 1401 and 1058 cm\(^{-1}\) are assigned to S=O str and S-O str, respectively which are characteristics stretching bands of organic sulphate [26]. Thus, from FTIR analysis the structure of 2-methyl-4-oxo-N-[(1Z)-1(sulphooxy) prop-2-ene-1-ylidene] penta-2-aminium (compound 3 in Scheme I) is confirmed.

**FTIR Analysis of Diacetone Acrylamide**

Figure 3 shows the peaks at 3280 cm\(^{-1}\) assigned to N-H str, at 3088 cm\(^{-1}\) corresponding to =C-H str, at 2899 cm\(^{-1}\) assigned to aliphatic C-H str, and at 1718 cm\(^{-1}\) and 1622 cm\(^{-1}\) are the characteristic absorption bands of keto (C=O str) and amide (CONH str) groups, respectively. Moreover, the peak at 1556 cm\(^{-1}\) is assigned to C=C str [26].
Figure 5. \(^1\)H NMR Spectrum of DAAM.

Confirmation of Cross-linking Reaction of DAAM Copolymer with 1, 3-Diaminopropane by FTIR

Figure 4 shows FTIR spectrum of DAAM copolymer (spectrum a) and cross-linking DAAM copolymers (spectra b and c). Carbonyl groups of DAAM readily react with 1,3-diaminopropane to form imines (C=N) and shows the characteristic IR absorption at 1623 cm\(^{-1}\) and indication of the cross-linking reaction taken place between the carbonyl group and 1,3-diaminopropane. It is also evident from the emulsion spectra that the absence of the carbonyl group (C=O) peak at 1713 cm\(^{-1}\) and amide peak at 1681 cm\(^{-1}\) and NH groups peak at 3325 cm\(^{-1}\) [26] confirm the cross-linking reaction.

\(^1\)H NMR Analysis of Diacetone Acrylamide

Figure 5 shows the arrangement of proton of diacetone acrylamide. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) : 1.4 (3H, s), 1.7 (3H, s), 2.1 (3H, s), 2.9 (2H, s), 5.5 (1H, d), 6.0 (2H, d), 7.2 (1H, s, -NH) ppm [26].

Mass Spectrometry of Diacetone Acrylamide

Figure 6 shows molecular-ion peak of DAAM at M/Z = 169 which indicates the formation of DAAM having molecular weight 169, the base peak (100% intensity) at M/Z = 58, and other fragments having M/Z = 154, 126, 112, 100, 84, 72, 55, 41, and 27, respectively [26].

Effect of DAAM Concentration on Particle Size and Particle Size Distribution of DAAM Copolymers

The particle size of DAAM copolymer emulsions increased with DAAM concentration, as DAAM has high affinity towards water, thus it migrates towards the aqueous phase bringing on this the size of micelles increases which lead to increase in particle size, and also it may stabilize latex like surfactants [21]. The bimodal particle size and particle size distribution of DAAM copolymer emulsions were observed with increased concentration of DAAM which resulted in diminished stability of the emulsions. The results of particle size and particle size distribution of DAAM copolymers at various concentrations of DAAM are summarized in Tables 2 and 3, respectively.

Effect of DAAM Concentration on Glass Transition Temperature of DAAM Copolymers

The DSC thermograms of the copolymers are shown

Table 2. Particle size of DAAM copolymers at various DAAM contents.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>DAAM in emulsion (wt%)</th>
<th>Particle size (µm)</th>
<th>Stability at room temperature (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10.41</td>
<td>312</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>10.65</td>
<td>312</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>11.60</td>
<td>377</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>15.42</td>
<td>232</td>
</tr>
</tbody>
</table>
in Figure 7. In copolymers, DAAM is polymerized with MMA and BA, wherein part of MMA is replaced with DAAM at 1 to 4 wt%. The glass transition temperature of MMA and DAAM are 100°C and 77°C, respectively. As the weight fraction of the soft monomer DAAM is increased, due to the decrease in the weight fraction of hard MMA monomer, this resulted in decrease in the glass transition temperature of the final copolymers from 27.06°C to 13.65°C.

**Effect of DAAM Concentration on Viscosity of DAAM-MMA-BA Emulsion**

Figure 8 shows the relation between concentrations of DAAM on viscosity of the emulsion. Hydrophilic DAAM contains carbonyl group which can form inter- and intramolecular hydrogen bonds with water molecules. The hydrogen bond formation of carbonyl groups of DAAM is enhanced in a manner which is proportional to DAAM concentration. In this way, molecular chains are compelled to overcome the strong hindrance when emulsion flows. Therefore, viscosity is increased with concentration of DAAM, and the viscosity increases to the highest values when the DAAM concentration is 4 wt%.

**Effect of DAAM Concentration on Film Properties of Its Cross-linked Copolymer Emulsion**

Dramatic improvement was observed in chemical and water resistance of DAAM copolymer sample containing 4 wt% of DAAM to cross-link with 1,3-diaminopropane, because 1,3-diaminopropane has hydrocarbon chain and two amino groups, and after cross-linking there are no such functionalities left to be susceptible to acid, alkali and water. Also, the cross-linked reaction of carbonyl group of DAAM and 1,3-diaminopropionate increases the molecular weight and provides denser polymer network on the substrate.

This is a unique monomer, which with increased DAAM weight percentage, two extreme properties viz; hardness and flexibility are also enhanced. Therefore, this monomer constitutes an important part in commercial thermosetting emulsions for wider

### Table 3. Particle size distribution of DAAM copolymers with varying DAAM contents.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Particle size distribution</th>
<th>DAAM concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D10%</td>
<td>1.35 μm</td>
</tr>
<tr>
<td>2</td>
<td>D50%</td>
<td>7.28 μm</td>
</tr>
<tr>
<td>3</td>
<td>D90%</td>
<td>25.14 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1 (wt%)</th>
<th>2 (wt%)</th>
<th>3 (wt%)</th>
<th>4 (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.11 μm</td>
<td>7.31 μm</td>
<td>27.90 μm</td>
<td>37.79 μm</td>
</tr>
<tr>
<td>1.87 μm</td>
<td>26.29 μm</td>
<td>10.57 μm</td>
<td>37.79 μm</td>
</tr>
<tr>
<td>1.51 μm</td>
<td>26.29 μm</td>
<td>37.79 μm</td>
<td>37.79 μm</td>
</tr>
</tbody>
</table>

**Figure 7.** DSC Thermogram of DAAM copolymer with varying amounts of DAAM concentrations.

**Figure 8.** Effect of DAAM concentration on viscosity of DAAM copolymer emulsions.
applications on a variety of substrates. The results of different film properties are summarized in Table 4.

**CONCLUSION**

We developed an efficient method for the synthesis of DAAM with good yield. Diacetone acrylamide copolymers were successfully cross-linked with 1,3-diaminopropane and characterized by FTIR. The results showed that the cross-linking reaction between the carbonyl group of DAAM and 1,3-diaminopropane yields an environmentally friendly reaction by which one component such as the thermoset emulsion cures at ambient temperature. The emulsion comprising of 4 wt% DAAM showed an increase in dry film thickness, viscosity and particle size. Also, dramatic improvement was observed in chemical and water resistance of cross-linked DAAM copolymer emulsions along with enhancement of the mechanical properties of the coatings.

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**REFERENCES**


