# Synthesis and Characterization of Crosslinked Polyurethane Dispersions Based on Hydroxylated Polyesters

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**ABSTRACT:** Stringent environmental regulation has endowed dispersible coatings with excellent property profiles in industrial applications. In this aspect, aqueous polyurethane dispersions (PUDs) are of special interest. The present study reports on the synthesis of hydroxylated polyester (HP) based polyurethane polyols containing internal carboxyl group with different diisocyanates. These polyurethane polyols were partly acetoacetylated with ethyl acetoacetate to incorporate $\beta$-ketoester in the polyurethane polyol backbone. The synthesized polyols were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, and differential scanning calorimetry. Polyurethane polyols and their acetoacetylated cousins were used to develop PUDs. Particle size of the reactive PUDs was evaluated by a particle size analyzer. PUDs were crosslinked with hexamethoxy methyl melamine and their film properties were studied by dynamic mechanical and thermal analyzers and thermogravimetric analyses. The effects of different diisocyanate and acetoacetylation on the stability of reactive dispersion and properties of the crosslinked films were evaluated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 368–380, 2006

**Key words:** hydroxylated polyester; diol structure; acetoacetylation; polyurethane; dispersion; thermal stability

## INTRODUCTION

To reduce volatile organic compound emissions, aqueous-based resins of polyurethane (PU) dispersed in water have attracted much attention in the literature.[1–4] These products exhibit many features related to conventional solvent-borne coatings with the advantage of having low viscosity at high molecular weight and good applicability. Aqueous polyurethane dispersions (PUDs), being nontoxic and nonflammable, are widely used as adhesives and coatings to a variety of substrates like textiles, metals, plastics, and wood.[5–8] Thus, preparation of two-component waterborne polyurethane in an aqueous system is more challenging than the solvent-borne system.[9,10] The

films prepared from such systems show excellent elasticity and abrasion resistance in addition to superior low-temperature impact resistance. An aqueous PUD is a binary colloidal system in which PU particles are dispersed in a continuous aqueous medium. One of the technical advantages of aqueous PUDs is that viscosity is independent of molecular weight of the polymer.[11] Thus, they can be prepared at a high solid content with a molecular weight high enough to form films with excellent performance.

Dispersible polymers can be prepared by incorporating hydrophilic ionic groups onto hydrophobic backbones. Such modified polymers can be readily dispersed into water under low shear stress with little or no external emulsifiers. However, to prepare high-molecular-weight polyurethane ionomer (PUI) dispersions, it is necessary to reduce polymer viscosity so as to facilitate dispersion. This can be achieved using an appropriate solvent like acetone or *N*-methyl-2-pyrrolidone or using elevated temperature to maintain the prepolymer in a molten state.[12] Properties of PUDs can thus be controlled by hydrophilicity of the polymer. Higher hydrophilicity leads to smaller average particle size and higher particle number. However,

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reaction conditions like temperature, stirring rate, addition rate of the components, and the order of their addition exert a considerable influence on the properties of the final products.

The effect of changes in chemical composition of PU has been studied extensively.[13–17] Dieterich and coworkers[5,18–20] have carried out extensive research on PUDs. Other important contributions have been made by Eisenberg,[21] Visser and Cooper,[22] Kim,[11] and Tirpark and Markusch.[23] Jang et al.[24] have prepared water-based PUDs and investigated the effect of process variables on molecular weight and mechanical properties by varying NCO/OH ratio, dimethylol propanoic acid (DMPA) content, and neutralization degree. Jhon et al.[25] have examined the influence of chain extension on PU particle size. However, the properties of PUDs can be modified by varying the composition of typical building blocks, such as polyols and polyisocyanate, or by chain extension. Even though PUDs with polyester backbones and DMPA have been widely used, still efforts are being made to improve their properties as well as to determine their structure–property relationships. Vogt-Birnbrich[26] synthesized reactive PUDs from acetoacetylated polyester polyol to study the importance of acetoacetylation in developing coatings formulations. Several studies have been made to develop PUDs by changing the experimental variables[27,28] and many strategies have been worked out for developing crosslinked PUDs.[29–38]

Our earlier studies on high solid PUs and polyester–melamine coatings have dealt with increase in solid content by partial accetoacetylation of the available hydroxyl groups in hydroxylated polyesters.[39–42] In the present study, we have adapted the acetoacetylated methodology to increase the solid content as well as adhesive properties of the reactive PUDs, since acetoacetyl groups have the capability to chelate with the metal ion upon application. In this work, we report the use of hydroxylated polyesters (HPs) as one of the building blocks to develop crosslinkable or curable reactive PUDs, which are rather different than the earlier systems that dealt with thermal[41] and weathering stability[42] of HP–hexamethoxy methyl melamine (HMMM) and HP-PU high solid coatings. In this study, HP is used to synthesize PU polyols containing internal carboxyl group with different diisocyanate structure. These PU polyols were partly acetoacetylated with ethyl acetoacetate to incorporate β-ketoester into PU polyol backbone. PU polyols and acetoacetylated PU polyols were used to develop the reactive PUDs. These PUDs were crosslinked with HMMM and their film properties were evaluated. The effect of different diisocyanate and acetoacetylation on the stability of reactive dispersion and properties of the crosslinked films were studied.

## EXPERIMENTAL

### Materials

Neopentylglycol (NPG) and 1,4-cyclohexanedimethanol from Eastman Chemical (New York, NY), trimethylolpropane (TMP) from Aldrich (Milwaukee, WI), DMPA, toluene diisocyanate (TDI: 9 : 1 ratio of 2,4 and 2,6 isomer), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI: mixture of Z and E isomer in 3 : 1 ratio) from Fluka Chemical (Ronkonkoma, NY), adipic acid (AA) from S.D. Fine Chemicals (Mumbai, India), isophthalic acid (IA), N,N-dimethylethanolamine (DEA) and triethyl amine (TEA) from SISCO (Mumbai), ethyl acetoacetate (EAA) from Ranbaxy (Mumbai), HMMM from Onward Chemicals (Mumbai), and polymeric diphenylmethane isocyanate (polymeric MDI) from ICI (Mumbai) were used. The melamine resin used in this study was a commercial grade sample with a degree of polymerization of 1.5, average molecular weight of 554, and average theoretical functionality of 8.3.

### Synthesis of resins for reactive PUDs

#### Synthesis of hydroxylated polyesters

A four-component HP of theoretical hydroxyl value 120 based on NPG (3.6 mol), TMP (0.15 mol), AA (2.7 mol), and IA (0.3 mol) was synthesized by the conventional melt condensation technique. The reaction was continued in a four-neck 2-L round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and dean-stark apparatus until the acid value of HP was less than 5. The HP was named HP1400.

### Synthesis of polyurethane polyols with internal carboxyl group

To synthesize PU polyol, a part of HP1400 melt was reacted with DMPA and TDI at 70–80 °C in a 500-mL four-neck round-bottom flask equipped with nitrogen inlet, mechanical stirrer, thermometer, and addition funnel until all isocyanate was consumed as monitored by FTIR. The acid value of the synthesized polyol was adjusted to 40 by the use of appropriate amounts of DMPA and the NCO/OH ratio was 1:1.4. The synthesized PU polyol was designated PUDT. In a similar way, other PU polyols were prepared by substituting TDI with MDI, HDI, and IPDI, which were named PUDM, PUDH, and PUDI, respectively. Resin characteristics are reported in Table I.

### Acetoacetylation of polyurethane polyols

Part of the PU polyols PUDT, PUDM, PUDH, and PUDM, respectively, were subjected to 40% aceto-

**TABLE I**
**Acid Value of HP1400 and $T_g$ of Polyurethane Polyols and Acetoacetylated Polyurethane Polyols**

| Resin | Acid value | $T_g$ (K) |
|-------|-----------|-----------|
| HP1400 | 3.6 | 218 |
| PUDT | 42 | 238 |
| PUDM | 38 | 240 |
| PUDH | 40 | 231 |
| PUDI | 42 | 235 |
| PUDTA | 46 | 229 |
| PUDMA | 44 | 231 |
| PUDHA | 46 | 226 |
| PUDIA | 48 | 228 |

acetylation of the available hydroxyl groups using a stoichiometric amount of EAA. The resulting aceto-acetylated PU polyols were named PUDTA, PUDMA, PUDHA, and PUDIA, respectively. For acetoacetylation, EAA was added to polyol melt at 80°C and the reaction temperature was raised to 140–150°C and continued until no distillate of ethanol was collected. The unreacted EAA and residue of ethyl alcohol were removed under vacuum.

### Preparation of reactive PUDs

PUDs of PU polyols and acetoacetylated PU polyols

Preparation of dispersions was done by an inverse process. The melt of PUDT along with the required amount of DEA to neutralize the incorporated car-boxyl group were added slowly to warm water (70–80 °C) and dispersed with a high-speed disperser. A calculated amount of TEA was added into the dispersion vessel to neutralize 20% of the free carboxylic acid groups on the PUD ionomer backbone. The mixture was stirred at the operating agitator speed for 1–2 h to complete the ionization and/or homogenization of the mixture. In a similar way, PUDM, PUDH, and PUDI were dispersed in water. Dispersions were designated according to their parent polyols. The synthetic step used to prepare the reactive PUDs is shown in Scheme 1.

### Characterization of resins for reactive PUDs

All synthesized resins were characterized by determining their acid value, solid content (SC), and pH. The SC is based on a w/w basis, i.e., weight of polyols added to weight of water. The pH was measured by a digital pH meter, while $T_g$ of the polyols was recorded from DSC thermograms. Samples were scanned from −40 to 200°C at a heating rate of 10 °C min$^{-1}$ in a nitrogen atmosphere at a flow rate of 30 mL min$^{-1}$. FTIR (Nicolet Spectrometer, FTIR-740) and $^1$H-NMR (Varian-Inova-500 MHz) spectra were recorded. A sample of about 20 mg was dissolved in 600 $\mu$L of CDCl$_3$ for $^1$H-NMR studies. FTIR had a resolution of 4

cm$^{-1}$ and 64 scans were averaged to obtain each spectrum.

### Particle size and morphology

PUDs were characterized by determining their particle size as measured by a Malvern (MAN-0247 Model, Malvern Instruments, UK) particle size analyzer. The instrument works with an optical unit consisting of a laser beam and a detector, which captures the actual scattering pattern from a field of particles. The instrument software utilizes Mie theory and the Franhaufer model to calculate the size of the particles that have created the pattern.[43] The wet cell Hydro 2000G/S/M was used for measurement. For comparison purposes, particle sizes of some of the PU polyol dispersions were determined from the SEM micrograph.

### Development of coating films from PUDs

The above synthesized and characterized PUDs were crosslinked with HMMM to develop clear coating films (see Scheme 1). All PUDs were mixed with HMMM in a 3 : 1 ratio based on solid content (w/w). HMMM was added slowly to PUDs under agitation. HMMM is not completely water soluble, but is water dispersible in the presence of water-dispersed resins. The crosslinking reactions were catalyzed with Na-cure 4167 (amine salt of acid phosphate in alcohol). These mixtures were used to prepare free and supported films of PUDs cured at 150°C for 40 min.

### Preparation of free film of coatings

The coatings were cast on the smooth surface of tin foil using a power-driven automatic applicator, which was kept in an oven at 150°C for 40 min. The supported coatings were placed in a clean mercury bath to amalgamate the tin substrate. The underside of the unsupported coating was cleaned of mercury or amalgam adhering to it.

### Dynamic mechanical properties

Dynamic mechanical analyses of the crosslinked PUD were carried out by DMTA IV (Rheometric Scientific) in tensile mode at a frequency of 1 Hz and 0.2% minimum strain with a heating rate of 3°C/min. In principle, DMTA detects the viscoelastic behavior of a polymer and yields quantitative results for the tensile storage moduli ($E'$) and the corresponding loss moduli ($E''$) as well as the loss factor (tan δ) as the quotient of loss and storage, $E''/E'$. $E'$ and $E''$ characterize the elastic and viscous components of a viscoelastic material under deformation.
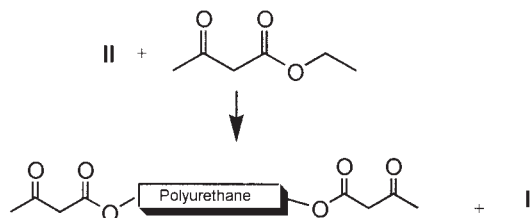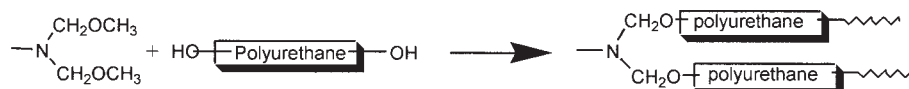
**Step 1.Synthesis of Hydroxylated Polyesters (I)**
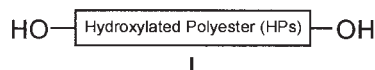
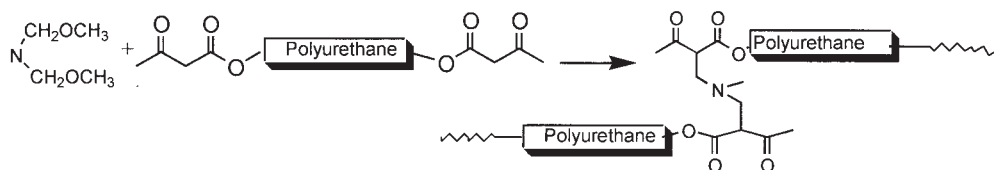**Step 2. Synthesis of Polyurethane Polyol (II) with internal Carboxyl group**
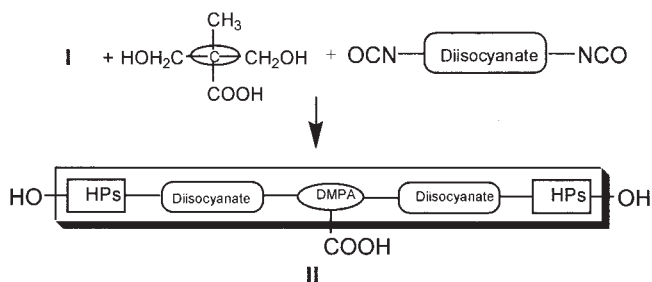
**Step 3. Acetoacetylation of Polyurethane Polyol**

**Step 4a. Crosslinking reaction of Polyurethane Polyol with HMMM**

**Step 4b. Crosslinking reaction of Acetoacetylated Polyurethane Polyol with HMMM**

**Scheme 1** Synthetic steps for the development of reactive polyurethane dispersions (steps 1–3) and crosslinking reaction of polyurethane dispersion with HMMM (steps 4a and b).

## Thermal stability and degradation kinetics

Dynamic thermogravimetric analysis of all coating films has been carried out using a Mettler Toledo TGA/SDTA 851$^e$ thermal system controlled by a computer at a heating rate of 20 °C min$^{-1}$ under a nitrogen atmosphere in the temperature interval 25–650°C. Sample weights were in the range of 9–10 mg (nitrogen flow rate of 30 mL min$^{-1}$). In TGA, the reaction rate is defined as the derivative of conversion with respect to time. The normalized TG curves were used for the percentage conversion evaluation. In the case of polymer degradation, kinetic analysis of thermo-gravimetric data from the weight loss curve is based on the kinetic equation given by

$$d\alpha/dt = k(1 - \alpha)^n, \qquad (1)$$

where $\alpha$ is the fraction of material decomposed at time $t$, $n$ is the reaction order, and $k$ is the rate constant. In TGA, the conversion is defined as the ratio of percentage mass loss of the sample after a certain time $t$ to the total mass in percent at the beginning of the experiment, i.e., $\alpha = (100 - wt)/100$, where $wt$ is sample mass in percent at time $t$. Combination of eq. (1) with the empirical Arrhenius expression gives

$$d\alpha/dt = Z \exp(-E/RT)(1 - \alpha)^n, \qquad (2)$$

where $Z$ is the pre-exponential factor, $E$ is activation energy of thermal decomposition, and $R$ is the gas constant. Introducing the heating rate, $\beta$, we get

$$d\alpha/dt = Z/\beta \exp(-E/RT)(1 - \alpha)^n. \qquad (3)$$

Equation (3) is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TG data.[44,45] Based on this expression, a number of methods have been developed to derive the kinetic parameters, $E$, $n$, and $Z$, from the thermogravimetric curves. In the present investigation, we have employed the methods of Broido,[46] Coats and Redfern,[47] and Chang[48] as discussed before.[45]

## RESULTS AND DISCUSSION

Waterborne urethane was designed to have carboxylic acid and hydroxy functionality. The polyols, viz., PUDT, PUDM, PUDH, and PUDI, have been synthesized to evaluate the effect of four different diisocyanate structures on the properties of PU polyols, PUDs, and their crosslinked films. While synthesizing PUDI and PUDH, dibutyltin-laureate was used as a catalyst, but in the case of PUDT and PUDM, no catalyst was used because TDI and MDI have a more reactive nature than IPDI and HDI. The reason for selecting DMPA is that it is one of the most widely used acids to prepare anionomeric dispersions. The acetoacetylated polyols like PUDTA, PUDMA, PUDHA, and PUDIA have also been synthesized to study the effect of acetoacetylation on the properties of PU polyols, PUDs, and their crosslinked films. The presence of a hydroxyl group in hydroxylated polyols allowed the possibility of crosslinking with HMMM, while the acetoacetylated polyols could form crosslinks with HMMM in two different ways as shown in steps 4a and 4b in Scheme 1. The methylene carbon atom of the $\beta$-ketoester moiety of acetoacetylated polyester is a
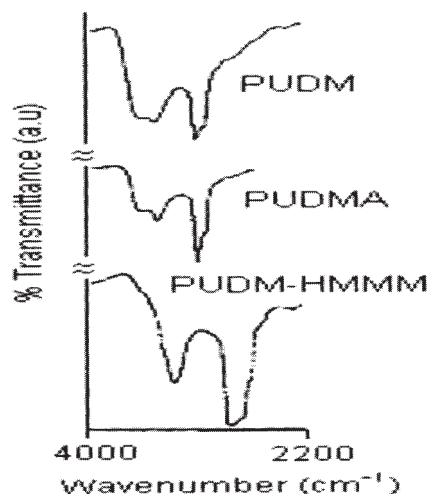


**Figure 1** Representative FTIR spectra of PUDM, the corresponding acetoacetylated counterpart PUDMA, and PUDM–HMMM films showing a decrease in intensity of –O-H band on acetoacetylation.

nucleophile because of keto-enol tautomerism and, therefore, crosslinking with HMMM may take place with the excess hydroxyl groups or with the $CH_2$ of the acetoacetylated part.

Representative FTIR spectra of PU polyol PUDM and its acetoacetylated counterpart are shown in Figure 1. There is not much difference in the spectra using different diisocyanates in synthesizing PU polyols. The FTIR spectrum of acetoacetylated HPs showed a significant decrease in intensity of the band between 3200 and 3600 $cm^{-1}$. This may be due to the partial replacement of –OH groups with the acetoacetate group as well as reduction of hydrogen bonding of HPs.

HP1400 and all the PU polyols were characterized by $^1$H-NMR. Representative NMR spectra of HP1400, PUDT, and acetoacetylated PUDTA are shown in Figure 2. The difference in $^1$H-NMR spectra upon reacting HP1400 with TDI to get PU polyol PUDT can be
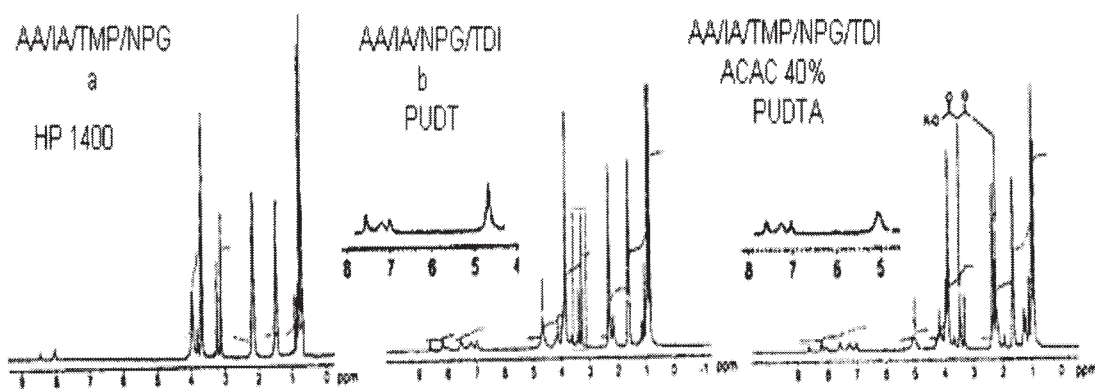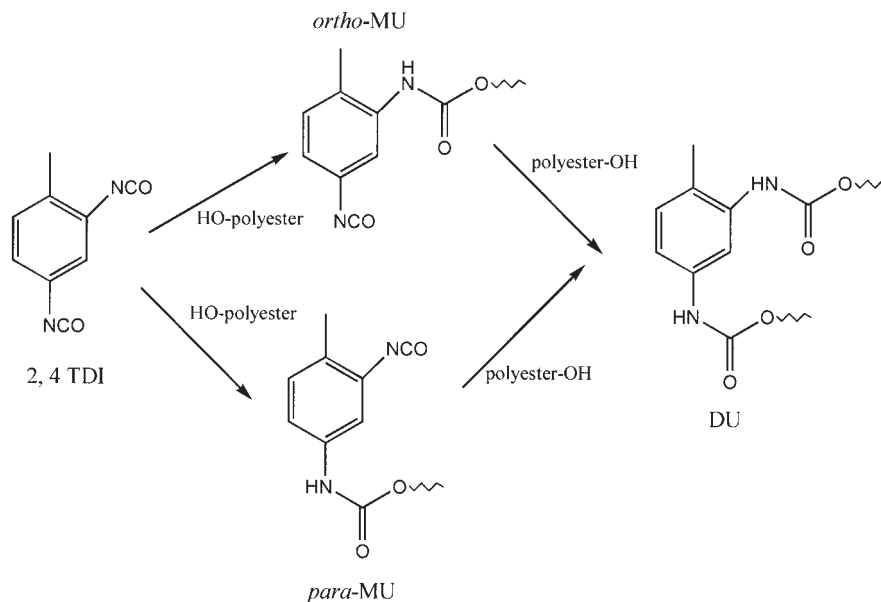


**Figure 2** $^1$H-NMR spectrum of HP1400, PUDT, and PUDTA.

**Scheme 2** Reaction between polyester polyol and 2,4-TDI.

seen in Figure 2(b). The major difference in the spectra is marked with an arrow and shaded area. However, the reaction of HP1400 with TDI to make PUDT resulted in the appearance of new peaks at 4.8, 6.9, and 7.2 ppm along with a decrease in intensity of –OH proton peaks at 3.4–3.6 ppm. The decrease in intensity signifies the reaction of –OH with –NCO. The new peak at 4.8 ppm (Fig. 2(b) and (c)] is due to the proton attached to carbon connected to urethane group –NH-COOC$H$ protons. TDI is an asymmetric aromatic diisocyanate and is an isomeric mixture, which contains a 9:1 ratio of 2,4- and 2,6-isomers. The two NCO groups attached to the aromatic ring are chemically different; one is bonded to the *ortho* position while the other is bonded to the *para* position. When TDI reacts with a polyester polyol, each TDI isomer provides two monourethanes (MU). As the reaction proceeds further, four MU are generated, which gives rise to two diurethanes (DU). Thus, eight different urethane moieties are formed during the reaction of TDI–polyester polyol, and these may be present in the product mixture. Peaks observed at 7.6 and 7.2 ppm are due to *ortho* and *para* NH of MU, respectively. The corresponding DU peaks appear around 7.3 and 6.9 ppm, respectively. The complicated reaction between 2,4-TDI and polyester polyol is shown in Scheme 2.

Similarly, in all other PU polyols, viz., PUDM, PUDH, and PUDI, new peaks appeared in the resonance area of 4.4–4.8 and 6.9–7.1 ppm, which confirms the urethane bond formation in all PU polyols, while in the case of PUDH and PUDI, there is no new resonance in the area of 8.0 ppm, which confirms the absence of aromatic ring protons. For IPDI-based systems, a new resonance occurred at 2.8 ppm, which is due to methylene attached to isocyanate and the cycloaliphatic ring.

A representative ^{1}H-NMR spectrum of acetoacetylated PU polyol of PUDT, i.e., PUDTA, is shown in Figure 2(c). Here, the major difference is the appearance of new resonance peaks at 2.3 and 3.5 ppm due to methyl and methylene protons, respectively, of the acetoacetate structure. The other difference observed was the upfield shift of –NHCOOC$H$ proton resonance from 4.7 to 5.1 ppm, which is due to the more electron-withdrawing nature of the acetoacetate group. Similarly, the shift of resonance peaks in all the other acetoacetylated systems occurred as per PUDMA (from 4.3 to 4.7 ppm), PUDHA (from 4.5 to 4.9 ppm), and PUDIA (from 4.5 to 5.2 ppm) along with the acetoacetate methyl and methylene resonances.

### Differential scanning calorimetric (DSC) analysis

The $T_g$ values of all the resins are reported in Table I. While synthesizing PU polyols using different diisocyanates, $T_g$ increased; for instance, during the preparation of PUDM from HP1400, $T_g$ increased from 218 to 240 K. The $T_g$ of PU polyols follows the order PUDM > PUDT > PUDI > PUDH, while upon acetoacetylation the trend is PUDMA > PUDTA > PUDIA > PUDHA.

The molecular weight builds up due to the chain extension of HP1400 with different isocyanates and also due to the presence of hard segments, i.e., urethane bonds leading to an enhancement of $T_g$. The higher $T_g$ of PUDM could be attributed to the presence of a greater number of ring structures in PU polyols as well as increased hydrogen bonding due to the sym-

**TABLE II**
**Solid Contents (SC) and pH of Polyurethane Dispersions Prepared from Polyurethane Polyols and Acetoacetylated Polyurethane Polyols at Different pH**

| PUDs | PUDT | PUDM | PUDH | PUDI | PUDTA | PUDMA | PUDHA | PUDIA |
|------|------|------|------|------|-------|-------|-------|-------|
| SC   | 36   | 36   | 36   | 36   | 40    | 40    | 40    | 40    |
| pH   | 8    | 8.2  | 7.8  | 8.2  | 8.3   | 7.9   | 8.2   | 8.1   |

metric nature of MDI. This is closely followed by PUDT, which contains ring structures as well as bulky methyl groups on the backbone, which restricts the movement of hard segments. The straight chain aliphatic structure of HDI has resulted in the lowest value of $T_g$ for PUDH, while the presence of cycloaliphatic ring and bulky methyl substituents led to enhancement of $T_g$ for PUDI compared to PUDH. The same trends follow for acetoacetylated polyols based on different diisocyanates, but as observed, acetoacetylation of PU polyols resulted in a lower $T_g$ than their corresponding unacetoacetylated systems. The reduction in $T_g$ and viscosity upon acetoacetylation is due to a reduction in hydrogen bonding and an increase in chain separation of different polyol moieties in the bulk.

### Polyurethane dispersions

The anionomeric reactive PUDs of all the above-discussed PU polyols and acetoacetylated PU polyols were prepared as discussed under Experimental. The very nature of the process results in the formation of a polymer colloid. The particle size distribution and their morphology have been studied. SC of the prepared PUDs from different PU polyols and acetoacetylated PU polyols at pH ~8 is shown in Table II and signifies a value range from 36 to 40%.

### Particle size analysis

The particle size distribution of PUDT, PUDH, PUDM, and PUDI was measured by particle size analyzer using distilled water as the dispersion medium. These data are displayed in Figure 3 and listed in Table III. PUDMA was more uniformly distributed and has a lower particle size range. The narrower the span, the more even the distribution of the particles. Based on the span data, all PUDs were polydisperse. This broad particle size distribution is attributed to the statistical nature of PU polyol chains. Upon acetoacetylation, polydispersity increased for all PU polyols due to the
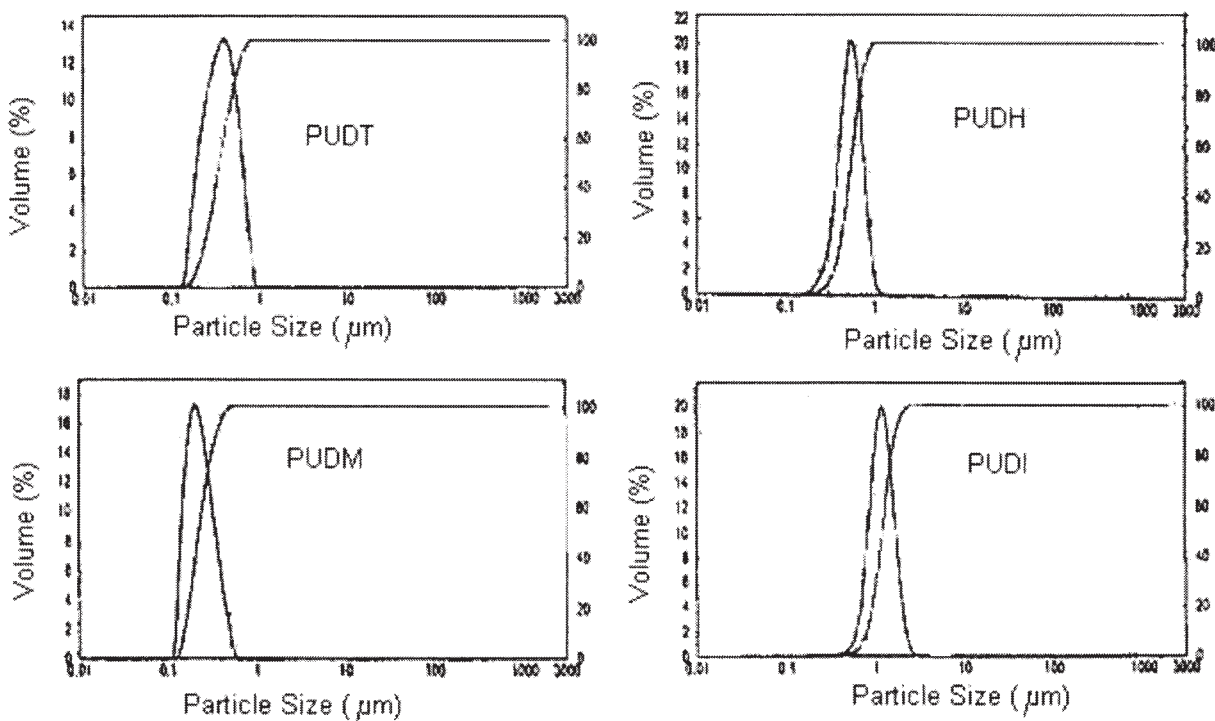


**Figure 3** Particle size distribution of PUDI, PUDH, PUDM, and PUDI measured by a particle size analyzer using water as the dispersion medium.

**TABLE III**
**Particle Size Distribution of Polyurethane Dispersions**

| System | Particle size distribution ($\mu$m) | | | Span | $D$ [4,3] ($\mu$m) | $D$ [3,2] ($\mu$m) |
| | $d$ (0.1) | $d$ (0.5) | $d$ (0.9) | | | |
|---|---|---|---|---|---|---|
| PUDT | 0.210 | 0.372 | 0.617 | 1.092 | 0.396 | 0.338 |
| PUDM | 0.154 | 0.227 | 0.370 | 0.948 | 0.47 | 0.332 |
| PUDH | 0.351 | 0.535 | 0.765 | 0.774 | 0.549 | 0.499 |
| PUDI | 0.801 | 1.199 | 1.740 | 0.783 | 1.241 | 1.125 |
| PUDTA | 0.161 | 0.246 | 0.436 | 1.118 | 0.276 | 0.240 |
| PUDMA | 0.138 | 0.188 | 0.265 | 0.677 | 0.196 | 0.184 |
| PUDHA | 0.602 | 1.443 | 6.159 | 3.850 | 3.804 | 1.219 |
| PUDIA | 0.359 | 1.169 | 3.381 | 2.585 | 1.656 | 0.812 |

$d$ (0.1), size of the particle below which 10% of the sample lies; $d$ (0.5), size of the particle below which 50% of the sample lies; $d$ (0.9), size of the particle below which 90% of the sample lies; span, width of distribution; $D$ [4,3], Volume-weighted mean; $D$ [3,2], surface-weighted mean.

presence of both polyol and acetoacetylated polyols in the system. The span data follows the order PUDT > PUDM > PUDI > PUDH and PUDHA > PUDIA > PUDTA > PUDMA.

The particle size of unacetoacetylated dispersions was in the range of 0.15 to 1.75 $\mu$m, while that of acetoacetylated HPs was in the range of 0.13 to 6.2 $\mu$m except for PUDI. However, the reported particle size of PUDs covers a broad range from 0.01 to 5 $\mu$m. Our data are well within this range except for PUDHA.[5,11,27] The broadness in distribution of particle size of PUDs could be the result of synthetic procedure involving step–growth polymerization followed by dispersion in water. Factors such as molecular weight, hydrophilicity of the backbone, and concentration of the stabilizing moiety might have also affected the extent of distribution of particles.

### Stability of PU dispersions

We have also observed the stability of all the PUDs. These observations were made on the basis of phase separation (water and resin layer) due to the complete particle settlement. A summary of these observations is presented in Table IV. These measurements were carried out in a sealed container on storage of the

prepared PUDs at room temperature (30–36°C). The highest stability was found for PUDMA, while the lowest stable system was PUDHA. It was earlier proposed[11] that ionomer dispersion can be stabilized due to the formation of electrical double layers between the ionic constituents, which are chemically bound to PU and their counterions, which migrate into water phase around the particles. The interference of electrical double layers of different particles resulted in particle repulsion, leading to the stabilization mechanism of dispersions as shown in Figure 4.

The well-known mechanisms of colloidal stabilization are electrostatic and steric stabilization or a combination of both. However, in ionomeric dispersions, colloidal stability might arise due to inbuilt stabilizing moieties in the polymer backbone. Since we have used

**TABLE IV**
**Stability of Polyurethane Dispersions**

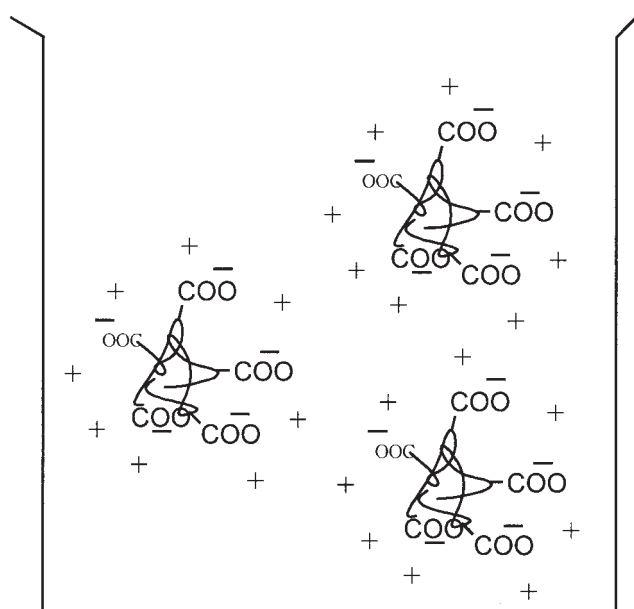| System | Particle settlement (days) | Phase separations (days) |
|---|---|---|
| PUDT | 8 | 20 |
| PUDM | 12 | 25 |
| PUDH | 29 | 90 |
| PUDI | 21 | 30 |
| PUDTA | 6 | 12 |
| PUDMA | 40 | (>6 months) |
| PUDHA | 1 | 7 |
| PUDIA | 3 | 12 |



**Figure 4** Schematic diagram of colloidal stabilization of anionic polyurethane ionomers in water.

the same stabilizing moieties in all dispersions, the difference in stability of the present systems is greatly influenced by the structure of the polyol backbone. Some of the dispersions started to phase separate after a short period, which may be due to lowered pH as a result of volatilization of neutralizing amine. These settled dispersions were redispersible by properly maintaining the pH and by mechanical stirring of the coagulated dispersion. However, the lowest stability of PUDHA may be due to its unusually high particle size when compared to other dispersions and, as a result, sedimentation occurs relatively early.

### SEM analysis

Morphology of the dispersed particles is important in determining the properties of the final coatings. To investigate the surface morphology of the dispersed particles, we have characterized the dispersions using SEM. From the representative SEM micrographs displayed in Figure 5, we find an increasing order of coagulation from PUDT to PUDHA; this supports the particle size study.

### Crosslinking of PUDs with HMMM to develop clear baked coatings

All dispersions were crosslinked with HMMM and films were cured at 150°C for 40 min. Film formation of the dispersions might be due to the evaporation of water and volatiles, which resulted in an increase of concentration of dispersed PU and HMMM particles. Due to coalescence these particles start reacting each other and, as a result, their cohesive strength will enhance significantly due to increased chain entanglement and secondary bonding, thus resulting in the formation of a solid cohesive film on the substrate. The physical appearance of the film is reported in Table V.

### FTIR spectra of polyurethane dispersions crosslinked with HMMM

FTIR spectra (4000–2200 cm$^{-1}$) of the representative HMMM crosslinked films of PUDM–HMMM are shown in Figure 1. The FTIR spectra of these films shows a sharp –NH stretching (due to PU polyol and bonded –NH resulting from the crosslinking of PUD-OH and melamine). A strong absorption peak of triazine ring observed at 815–830 cm$^{-1}$ confirms the presence of melamine in the films.

### Dynamic mechanical properties and film properties of PUDs-HMMM films

DMTA spectra of the free films of all the crosslinked PUDs-HMMM are shown in Figure 6, while the dynamic mechanical properties are listed in Table VI. All
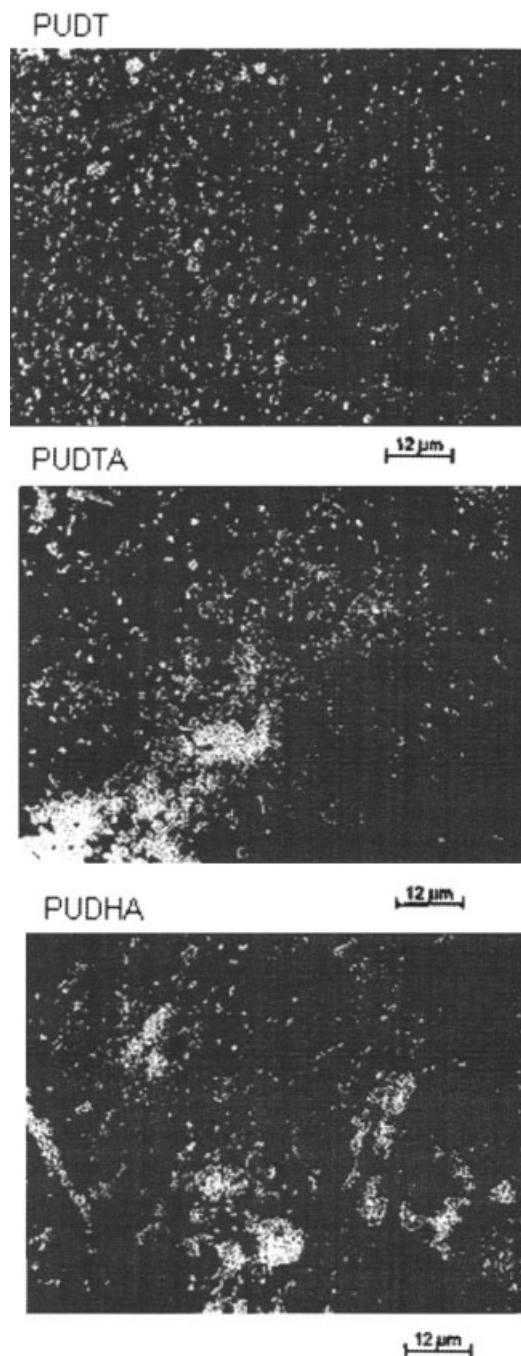


**Figure 5** Representative SEM micrographs [×2.5 K] of PUDT, PUDTA, and PUDHA.

the scans shown in Figure 6 clearly indicate an increase in $E'$ after 150°C, which is a typical characteristic of the melamine-based coatings. This further supports the results from the cure study and the hydroxylated polyester–HMMM film properties as discussed before.[39–42] A steep drop in $E'$ was observed in all spectra, which signifies the flexible nature of the films. The tan δ peaks also indicated the flexible nature of the films. However, PUDH and PUDHA films exhibited sharp tan δ peaks in the spectra (see Fig. 6(a), inset).

**TABLE V**
**Physical Appearance of Polyurethane Dispersions Crosslinked with HMMM**

| PUDs | PUDT | PUDM | PUDH | PUDI |
|---|---|---|---|---|
| Color | Yellow (slight) | Yellow (medium) | Transparent | Transparent |
| Appearance | Flexible | Flexible | Highly flexible | Flexible |
| PUDs | PUDTA | PUDMA | PUDHA | PUDIA |
| Color | Yellow (medium) | Yellow (dark) | Yellow (slight) | Yellow (slight) |
| Appearance | Flexible | Flexible | Highly flexible | Flexible |

This observation indicates that these films are more flexible than the remaining PUD–HMMM films. The $T_g$ values of PUDH and PUDHA were 25 and 36°C, respectively, which suggests that upon accetoacetylation crosslinking density increased. Comparing the $E'$ (30 °C) values as shown in Table VI, which are indirectly regarded as a measure of hardness, PUDIA and PUDMA films were found to be superior to other films. The $E'$ (30 °C) and $T_g$ values for PUDIA and PUDMA were $4.57 \times 10^8$ Pa., 69°C, and $2.86 \times 10^8$ Pa., 92°C, respectively, and were higher than for the other crosslinked PUDs.

The value of tan $\delta_{max}$, i.e., peak height, is a direct measure of curing and crosslink density. The lower the height of tan $\delta_{max}$, the higher the crosslink density of the system. Based on this, a similar crosslink density was found for PUDM, PUDT, PUDH, and PUDIA. Based on the overall comparison, PUDIA and PUDMA are tougher films than others. Even though some of the dynamic mechanical properties were inferior, the basis of their selection is their higher room temperature modulus and crosslink density. It is thus difficult to assign any specific reason, but in general, it can be concluded that upon acetoacetylation, there is
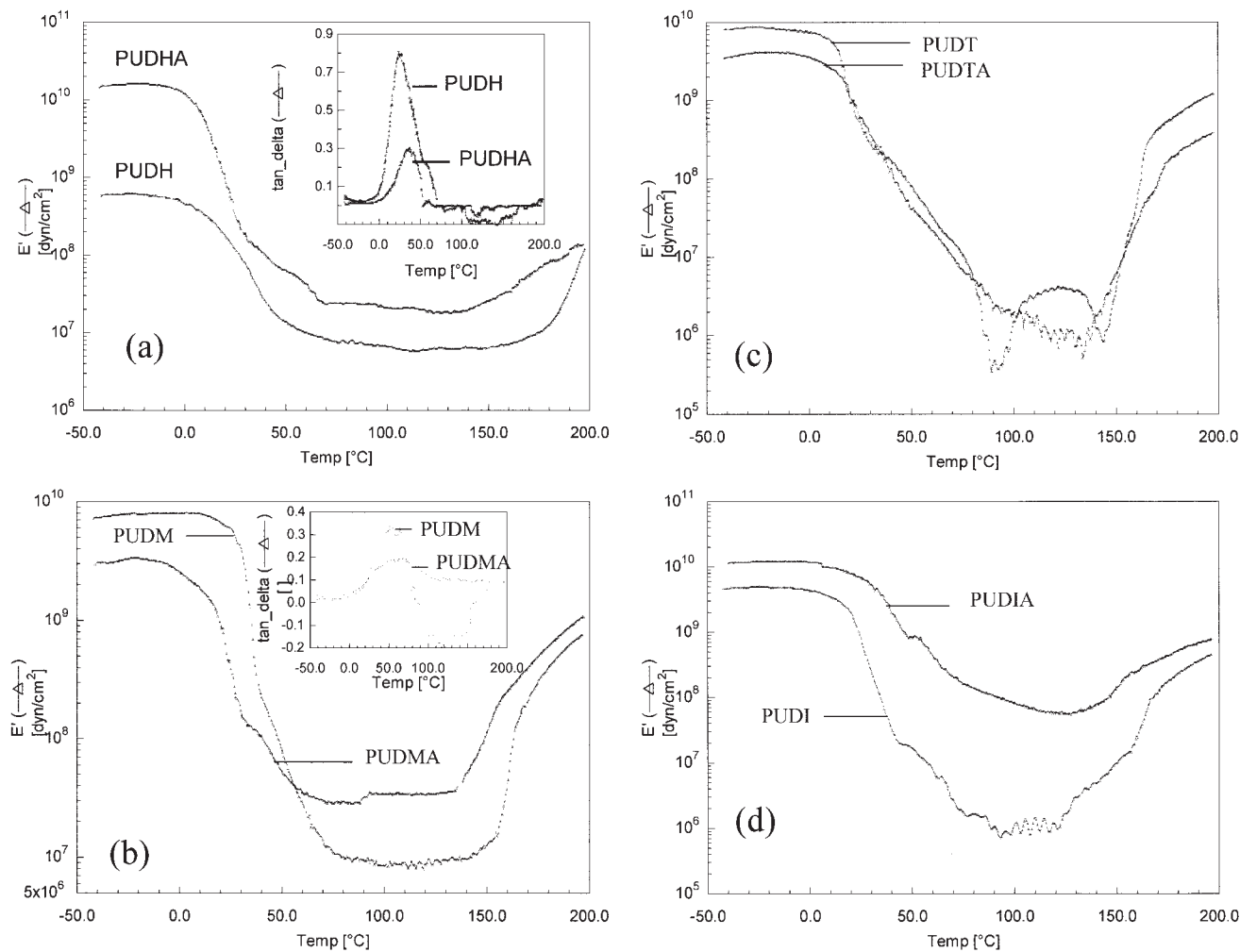


**Figure 6** DMTA spectra of unacetoacetylated and acetoacetylated coatings.

**TABLE VI**
**Dynamic Mechanical Properties of PUD Films Crosslinked with HMMM**

| Films | $E' \times 10^{-7}$ Pa. (30°C) | $T_g$ (°C) | tan $\delta_{max}$ | $v_e \times 10^4$ (mol/cm³) | $M_c$ (g/mol) |
|-------|-------------------------------|------------|--------------------|-----------------------------|---------------|
| PUDM  | 5.58  | 56 | 0.33 | 1.35  | 3153  |
| PUDT  | 2.65  | 67 | 0.31 | 1.48  | 7429  |
| PUDH  | 0.74  | 25 | 0.8  | 0.6   | 18419 |
| PUDI  | 2.17  | 40 | 0.40 | 2.25  | 4894  |
| PUDMA | 28.6  | 92 | 0.57 | 12.6  | 890   |
| PUDTA | 2.6   | 36 | 0.65 | 6.35  | 1700  |
| PUDHA | 1.7   | 36 | 0.32 | 0.79  | 13647 |
| PUDIA | 45.7  | 69 | 0.31 | 18.1  | 595   |

an increase in crosslink density of the film, as shown in Figure 6. To have a better understanding, we have taken $E'_{min}$ ($\gg T_g$) so that a generalization can be made and crosslink density ($v_e$), as well as molar mass between crosslinks. $M_c$ can be calculated (see Table VI) using the kinetic theory of rubber elasticity using eqs. (4) and (5):

$$\nu_e = E'/3RT, \qquad (4)$$

where $R$ is the universal gas constant and $T$ is temperature ($T > T_g$).

$$M_c = \rho/\nu_e, \qquad (5)$$

where $\rho$ is the density of coating films, determined experimentally by displacement method (found to be in the range of 1.03–1.15 g/cm³ of all the coating films).[39,40]

Generally, the higher the crosslink density the lower the elastically effective chain length ($M_c$) and the harder the film, whereas flexibility is best in noncrosslinked resins. Based on crosslink density and $M_c$ values, PUDMA ($v_e$ is $1.26 \times 10^{-3}$ mol/cm³) and PUDIA ($v_e$ is $1.81 \times 10^{-3}$ mol/cm³) are better crosslinked systems than others. Overall, the present results indicate that the rigid nature of diisocyanate structure of PUDM and PUDI is responsible for their superiority, while the straight chain structure of HDI accounts for the poor properties of PUDH and PUDHA.

### Thermal stability and kinetic parameters of PUDs

Representative TG thermograms of crosslinked PUDs are shown in Figure 7 and thermal decomposition data obtained from TG and DTG (figures not shown) are reported in Table VII. The TGA curve shows two distinct regions of degradation. A negligible weight loss occurred around 100–120°C, due to the release of adsorbed or entrapped moisture. The first step of decomposition is between 180 and 340°C, whereas the second step lies between 340 and 445°C. Around 70–80% of samples decomposed above 450°C. The first onset value, $T_{1id}$, and the second onset value, $T_{2id}$, the temperature at which degradation rate is highest, $T_{max}$, and the endset temper-

ature, $T_{df}$, showed that PUDM is most stable among the unacetoacetylated series, while PUDH is the least stable. The order of stability has the trend PUDM > PUDT > PUDI > PUDH. For instance, the $T_{max}$ and $T_{df}$ values of PDDM and PUDH were 392 and 425°C and 376 and 432°C, respectively, while the corresponding values for PUDT and PUDI fall between these data. The aromatic nature of MDI and TDI imparts rigidity in the polyol structure, which will result in enhanced thermal stability, whereas the aliphatic nature of HDI results in chain flexibility. The cycloaliphatic ring with methyl branching of IPDI makes PUDI more stable than PUDH, but the second step of decomposition is faster due to the presence of bulky methyl groups, as seen from a steep fall in the TG curve. These bulky methyl groups due to branch
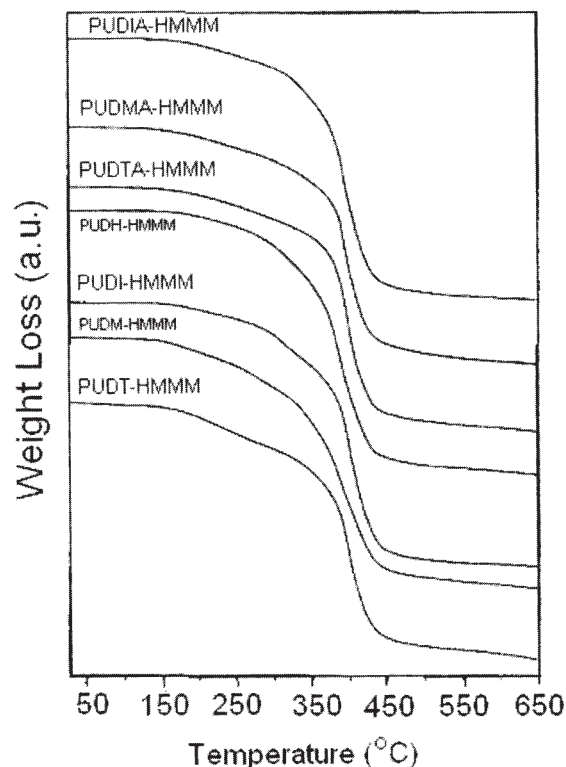


**Figure 7** TG thermograms of HMMM crosslinked PUD films.

**TABLE VII**
**Thermal Decomposition Data of PUDs Crosslinked with HMMM**

| Sample | $T_{1id}$ (°C) | $T_{2id}$ (°C) | $T_{max}$ (°C) | $T_{df}$ (°C) | % Conversion at 300°C | % Conversion at 450°C |
|--------|------|------|------|------|------|------|
| PUDM | 198 | 371 | 392 | 425 | 10.78 | 77.32 |
| PUDT | 179 | 367 | 389 | 423 | 11.79 | 77.16 |
| PUDI | 191 | 333 | 386 | 419 | 17.15 | 82.65 |
| PUDH | 178 | 326 | 376 | 432 | 14.70 | 82.41 |
| PUDMA | 183 | 374 | 391 | 416 | 10.99 | 71.56 |
| PUDTA | 166 | 350 | 380 | 404 | 8.43 | 72.37 |
| PUDIA | 186 | 318 | 388 | 416 | 9.44 | 81.35 |
| PUDHA | 187 | 324 | 373 | 444 | 17.87 | 82.14 |

chain scissioning might have facilitated decomposition, thereby making PUDI less stable than PUDT.

Data interpretation for the acetoacetylated series is somewhat difficult. On the basis of percentage conversion values of 17.87 and 82.14, respectively, at 300 and 450°C, we could conclude that PUDHA is the least stable, while PUDMA, PUDTA, and PUDIA have the same range of stability. Once we compare the thermal stability of any unacetoacetylated and the corresponding acetoacetylated coatings, theoretically we should expect an increase in characteristic thermal decomposition data, but from the scattered data reported in Table VII, it is rather difficult to achieve such a conclusion. Representative Chang, Coats–Redfern, and Broido plots are shown in Figure 8. Calculated activation energy and other kinetic parameters are reported in Table VIII. Activation energy values of PUDM, as calculated from the Broido, Coats–Redfern, and Chang methods, were 61.7, 39.3, and 107.8 kJ/mol, respectively, suggesting a dependency of $E$ values on the method used to evaluate the data.[45] Activation energy values calculated from Broido, Coats–Redfern, and Chang equations have shown the highest stability of PUDM, which was 61.7, 39.3, and 107.8 kJ/mol., respectively, and this supports the above observations for unacetoacetylated systems. Activation energy order calculated from Broido, Coats–Redfern, and Chang methods in the case of acetoacetylated series supports the theoretical prediction of higher stability in comparison to that of the corresponding unacetoacetylated PUDs, PUDM, PUDT, and PUDI. For instance, in the case of PUDM and PUDMA, $E$ values calculated from the Broido equation were 61.7 and 62.2 kJ/mol, respectively, but for HDI-based PUD coatings, the $E$ value was smaller for acetoacetylated coatings (PUDHA) than its unacetoacetylated counterpart (PUDH). However, at this stage, we are not in a position to advance any comment about the cause for such a reverse order of stability. The order of decomposition ($n$) in the Chang method as calculated by the least-squares fit was 1.9–2.5 for unacetoacetylated coatings and 1.9 to 2.8 for the corresponding acetoacetylated PUDs. The ln $Z$ values for the Chang method were in the range of 22.8–40.3. Correlation coefficient values in all equations were greater than 0.96.

## CONCLUSIONS

Because of their excellent mechanical properties, waterborne PUDs are used in many application areas. In this study, results are presented for the syntheses of aqueous PUDs without the use of organic solvents. PUDs developed in this study offer good balance between thermomechanical and mechanical properties
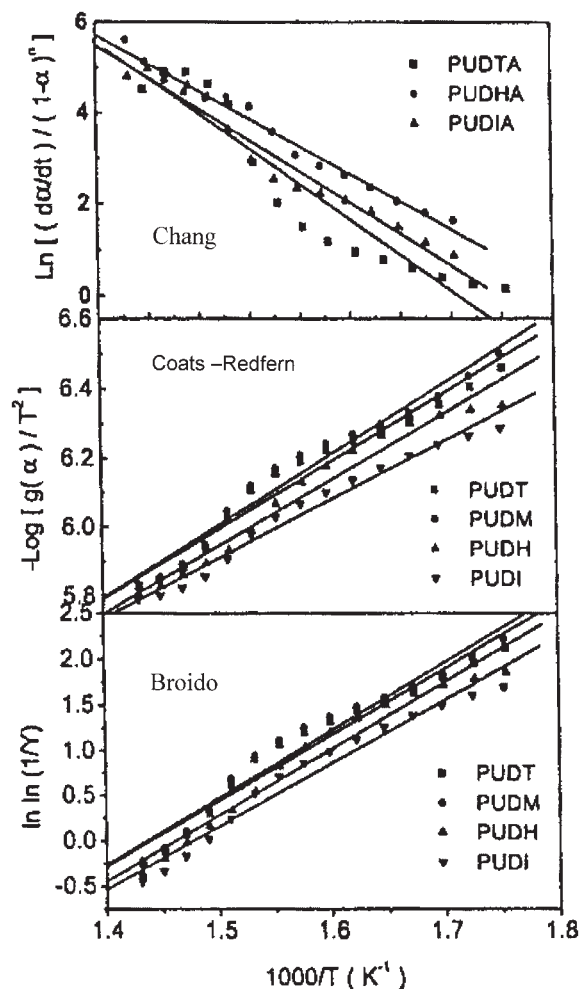


**Figure 8** Representative Chang, Coats–Redfer, and Broido plots for the thermal degradation kinetics of polyurethane dispersions.

**TABLE VIII**
**Kinetic Parameters Calculated from Different Equations**

| Sample | Broido | | Coats–Redfern | Chang | | |
|---|---|---|---|---|---|---|
| | $E$ (kJ/mol) | $r^2$ | $E$ (kJ/mol) | $E$ (kJ/mol) | $ln\ Z$ | $n$ |
| PUDM | 61.7 | 0.96 | 39.3 | 107.8 | 23.7 | 2.5 |
| PUDT | 60.6 | 0.97 | 37.8 | 106.7 | 23.5 | 2.4 |
| PUDI | 57.9 | 0.97 | 32.5 | 105.5 | 23.4 | 2.0 |
| PUDH | 60.9 | 0.96 | 36.7 | 105.1 | 24.9 | 1.9 |
| PUDMA | 62.2 | 0.97 | 38.9 | 190.3 | 40.3 | 2.8 |
| PUDTA | 61.4 | 0.99 | 39.5 | 129.3 | 27.3 | 2.8 |
| PUDIA | 73.4 | 0.98 | 48.4 | 114.8 | 24.8 | 1.9 |
| PUDHA | 52.4 | 0.99 | 31.5 | 101.5 | 22.8 | 2.5 |

as well as film-forming properties. Properties of PUDs were modified by varying the composition of typical building blocks, such as polyols and polyisocyanates, or by acetoacetylation. Eight reactive PUDs differing in diisocyanate structure have been prepared from HP1400 and DMPA and characterized by FTIR and $^1$H-NMR analyses. The difference in coating structure was effected using different diisocyanate moieties and partial acetoacetylation of the hydroxyl group. PUDs were crosslinked with HMMM to evaluate their dynamic, mechanical, and thermal stability properties. PUDMA-based dispersions have a finer particle size. Upon acetoacetylation, a uniform increase in crosslinked density of PUD–HMMM films was observed. PUIA–HMMM film was superior to others. Thermal stability study indicated the superior properties of PUDM–HMMM systems compared to others.

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