

## Performance of Novel Hyperbranched Poly(aryl-ether-urea)s Doped with N3-Dye in Nanocrystalline DSSC

Subramaniyan Sathiyaraj,<sup>1</sup> Mahalingam Vanjinathan,<sup>2</sup> A. Shanavas,<sup>3</sup> Subramaniyan Amudha,<sup>4</sup> S. Austin Suthanthiraraj,<sup>4</sup> A. Sultan Nasar<sup>1</sup>

<sup>1</sup>Department of Polymer Science, University of Madras, Guindy Campus, Chennai 25, Tamil Nadu, India

<sup>2</sup>PG and Research Department of Chemistry, D. G. Vaishnav College, Chennai 106, Tamil Nadu, India

<sup>3</sup>Chemical, Metallurgical and Material Engineering, Polymer Technology Division, Tshwane University of Technology, Pretoria, South Africa

<sup>4</sup>Department of Energy, University of Madras, Guindy Campus, Chennai 25, Tamil Nadu, India

Correspondence to: A. S. Nasar (E-mail: drasultannasar@yahoo.com or drasultannasar@unom.ac.in)

**ABSTRACT:** An amine-terminated hyperbranched poly(aryl-ether-urea) (HBPEU) was prepared from an AB<sub>2</sub>-type blocked isocyanate monomer and then its end groups were modified into urea (M-HBPEU) by reaction with phenyl isocyanate. Both of the polymers were doped with N3-dye along with KI/I<sub>2</sub> to work as efficient polymer electrolytes in nanocrystalline dye sensitized solar cell. The increment in the conductivity of doped HBPEU and doped M-HBPEU was very significant and reached its value at  $8.2 \times 10^{-3}$  and  $4.1 \times 10^{-2}$  S/cm, respectively. The current–voltage (*I*–*V*) characteristics of these two doped polymers measured under simulated sunlight with AM 1.5 at 60 mW/cm<sup>2</sup> generate photocurrent of 2.5 and 3.6 mA/cm<sup>2</sup>, together with a photo voltage of 690 and 750 mV, and fill factor of 0.55 and 0.61 yielding a overall energy conversion efficiency of 2.4% and 4.1%, respectively. These results suggest that M-HBPEU show better cell performance and conductance properties than the HBPEU. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40408.

**KEYWORDS:** blocked isocyanate monomer; hyperbranched poly (aryl-ether-urea); polymer electrolyte; ion conducting polymer; dye sensitized solar cell (DSSC); photovoltaic applications

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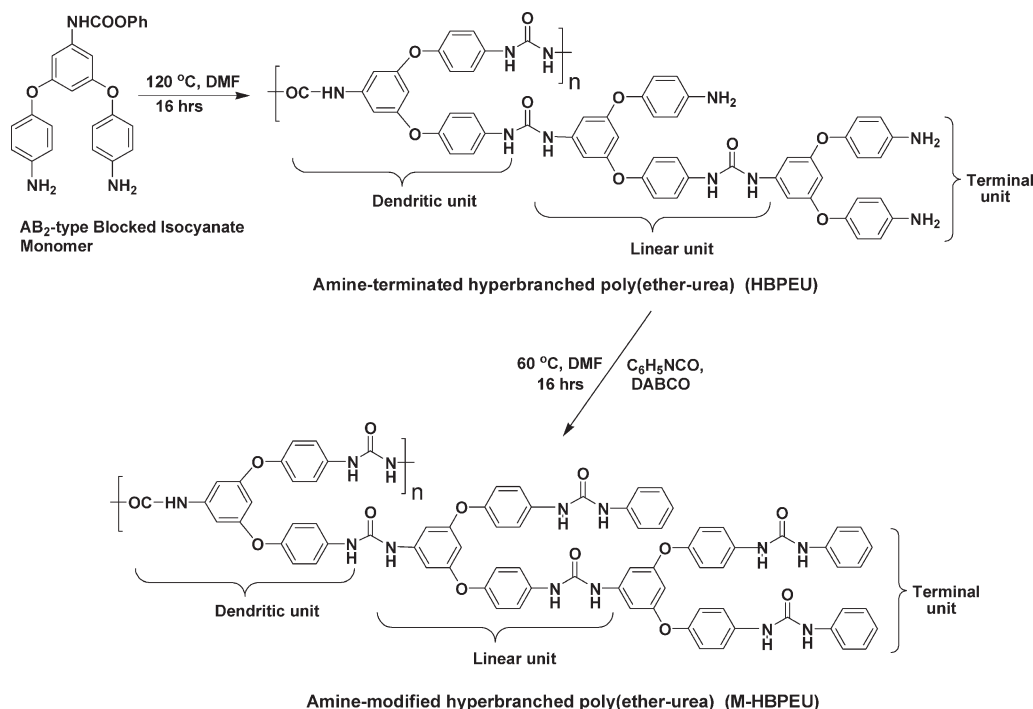
### INTRODUCTION

Polymer electrolytes containing alkali metal salt have received much interest towards their applications in dye-sensitized solar cells (DSSCs). They are known to possess appreciable values of ionic conductivity and overcome certain problems like sealing and solvent leakage. More recently, polymer blending has also been found to offer a feasible tool instead of employing a single polymer matrix thereby yielding combined advantages of various components of individual polymers. One of the major problem existing in the case of a DSSC concerns with its electrochemical stability and related storage characteristics. Therefore, attempts have been pursued towards addressing such technological aspects for ultimately improving their device performance.<sup>1–5</sup>

Hyperbranched polymers (HBPs) are unique macromolecules, which have consecutive branching point in their repeat units and many terminal functional groups.<sup>6–9</sup> As analog to dendrimers, HBPs have a three-dimensional architecture in contrast to linear polymers. Large number of functional groups present

in HBP could allow fine-tuning of the properties. The viscosity of HBP is generally low even if the molecular weight is high enough due to the lack of chain entanglements. One of the potential advantages of HBP lies in its production process: HBP can be prepared by the one step polymerization of the designed monomers. Therefore, mass production of HBP can easily be achieved in contrast to dendrimers. It is reported that the introduction of branching point to the rigid aromatic polymers results improved solubility, low viscosity, and low crystallinity.<sup>10</sup> Moreover, they prefer to show globular structure, with the terminal groups on the surface when the molecule is built to some degree of polymerization.<sup>11</sup> By controlling the nature of the end groups of the HBPs, it is possible to endow these polymer architectures with functions such as enhanced adhesion and energy harvesting as well as optoelectronic characteristics.

Aromatic polyurea dendrimers containing ether connectivity exhibit good thermal stability and optical property.<sup>12</sup> Polymers containing aryl-ether connectivity also exhibit good ionic conductivity.<sup>13</sup> The presence of ionic conductivity in combination



**Scheme 1.** Synthesis of amine- and phenylurea-terminated hyperbranched poly(aryl-ether-urea)s.

with good thermal stability is an important requirement for a material to be used for photovoltaic devices. Recently, we reported hyperbranched poly(aryl-ether-urethane)s and hyperbranched polyurethanes containing azomethine and aryl-ether connectivity for solar cell applications.<sup>14,15</sup>

There are only a few articles describing the study of hyperbranched poly(ether-ureas).<sup>16–18</sup> In this work, we report two types of hyperbranched poly(aryl-ether-urea), one which contains a large number of peripheral amine functional groups (HBPEU) and the other one is a amine-modified-into urea linkages using phenyl isocyanate (M-HBPEU) (Scheme 1). In these polymers, the presence of lone pair on the nitrogen and carbonyl oxygen atoms of urea linkages and oxygen atoms of ether linkages attached to aromatic rings increases the conjugation length. Besides, these lone pair electrons can readily interact with the metal cations added and hence increase the conductivity and the performance of DSSCs. These polyureas are expected to show better cell performance than the polymers reported in our previous work,<sup>14,15</sup> because of the presence systems, the two aromatic rings are separated by oxygen atom of ether linkage or by urea linkage instead of alkyl groups; the presence of alkyl groups restricts the conjugation length and ionic conductance.

## EXPERIMENTAL

### Materials

Diazabicyclo(2,2,2)octane (DABCO) (Lancaster), potassium iodide (Merk), iodine (Merk), and phenyl isocyanate (Aldrich) were used without further purification. DMF was purified by refluxed with calcium hydride and distilled under reduced pressure. 3,5-Bis (4-aminophenoxy)phenyl phenylcarbamate (AB<sub>2</sub>-monomer) was prepared using the reported procedure.<sup>16</sup>

[cis-Dithiocyanato-*N,N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)] dihydrate (N3 dye) was obtained from Aldrich and used as received.

### Measurements

The Fourier transform infrared (FTIR) spectra of samples were recorded by the KBr pellet method on a ABB-Bomem FTIR spectrometer. The UV–vis spectra were recorded on a Shimadzu 260 spectrophotometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the polymers were recorded using a Bruker 300 MHz spectrometer, tetramethylsilane (TMS) was used as an internal standard. Differential scanning calorimetry experiments (DSCs) were performed using NETZSCH–DSC200F3 equipment. The experiments were performed in nitrogen atmosphere at a heating rate of 10 °C/min; the cooling rate was 20 °C/min. Thermogravimetry (TGA) was performed using SDT Q600 V8.0 (TA Instruments) under nitrogen atmosphere at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) measurements were made on a Waters liquid chromatograph equipped with a 410 differential refractometer (RI detector). DMF containing 0.01% lithium bromide was used as an eluent at a flow rate of 1 mL/min. Styragel columns of pore size 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å were used. The molecular weight calibrations were performed using polystyrene standards having molecular weight (*M<sub>w</sub>*) in the range of 2.9 × 10<sup>3</sup>–5.7 × 10<sup>5</sup>. X-ray diffraction (XRD) analyses were performed using Bruker Axs Model D8 Advance X-Ray Diffractometer with CuKα monochromatized radiation at 25 °C (tube voltage: 40 kV; tube current: 30 mA, and λ: 1.541 Å). The samples were scanned from 2θ = 10°–80°.

The scanning electron microscopic (SEM) studies were performed using a SEM, Hitachi-S 3400N Model with an applied

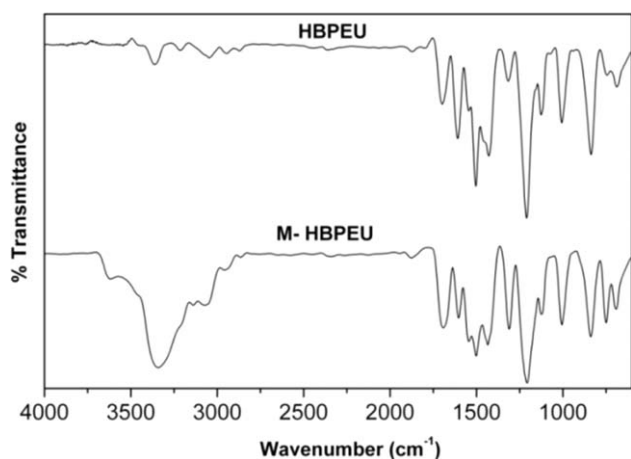


Figure 1. FTIR spectra of hyperbranched polyurea.

accelerating voltage of 15 kV. Electrical conductivity of the polymer samples was evaluated by impedance spectroscopy in the frequency range 20 Hz to 1 MHz using HP4284A Precision LCR Meter and the impedance data were analyzed by means of Boukamp equivalent circuit program software available internally during each measurement. The samples were placed in between two silver non-blocking electrodes and the conductivity of the sample was calculated using the relation  $\sigma = t/A \times R_b$ , where  $t$  is the thickness of the sample,  $R_b$  is the bulk resistance, and  $A$  is the contact area of cross-section of the sample.

The current–voltage ( $I$ – $V$ ) curves for DSSCs were measured at AM 1.5 illumination using a BAS100A Electrochemical Analyzer under an illumination area of 1 cm<sup>2</sup> with tungsten halogen lamp (OSRAM, Germany) of light intensity 40 mW/cm<sup>2</sup> with power of 150 W.

#### Preparation of Amine-Terminated HBPEU

The monomer (1.2 g [2.8 mmol]) was dissolved in 12 mL of dry DMF; the solution was heated to 120°C with stirring under nitrogen atmosphere for 16 h. After the reaction time was over, the reaction mixture was cooled to room temperature and the poly-

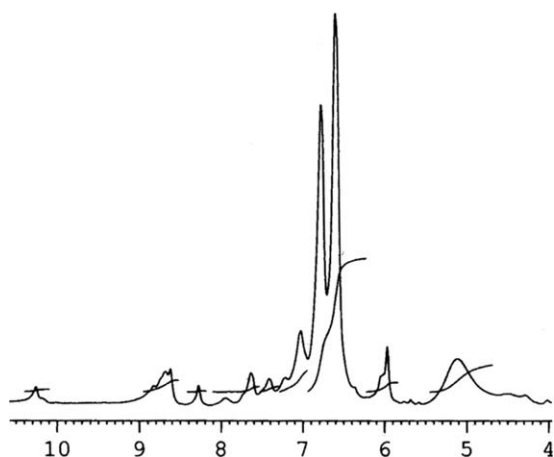


Figure 2. 300 MHz <sup>1</sup>H-NMR spectrum of amine-terminated HBPEU in DMSO-*d*<sub>6</sub>.

mer was precipitated in 1 L of water. The polymer was filtered, washed with water, and dried *in vacuo* at 90°C to constant weight.

Yield: 0.66 g (71%). IR (cm<sup>-1</sup>, KBr) 3356 (–NH stretching), 1682 (urea C=O), 1605 (aromatic), 1551 (–NH bending), 1203, and 1119 (C–O–C). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  10.2, 8.83, and 8.27 (s, urea NH), 5.96–7.94 (m, aromatic), 5.10 (br., –NH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  160.3, 145.3, 145.0, 121.1, 120.7, 119.9, 114.9, 99.5.

#### Preparation of End-Group Modified HBPEU

Phenyl isocyanate (0.39 mL [3.568 mmol]) and 0.014 g of DABCO were added at room temperature to a solution of amine-terminated HBPEU prepared in a separate experiment. The solution was heated to 60°C with stirring under nitrogen atmosphere for 16 h. After the reaction time was over, the reaction mixture was cooled to room temperature and the polymer was precipitated in 1 L of water. The polymer was filtered, washed with water, and dried *in vacuo* at 90°C to constant weight.

Yield: 1.08 g (86%). IR (cm<sup>-1</sup>, KBr) 3364 (–NH stretching), 1659 (urea C=O), 1597 (aromatic), 1551 (–NH bending), 1203 and 1119 (C–O–C). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  10.2, 8.81 and 8.27 (s, urea NH), 6.06–7.61 (m, aromatic). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>): 159.3, 152.6, 150.2, 144.6, 139.7, 136.5, 134.6, 128.7, 121.7, 120.2, 119.7, 118.1.

#### Preparation of Polymer Electrolyte for the Fabrication of DSSC

Polymer electrolyte solution was prepared by suspending 0.1 g of synthesized polymer, 0.03 g of KI, and 0.009 g of I<sub>2</sub> in 25 mL of DMF and the solution was stirred at 60°C for 3 h to obtain a homogeneous mixture. This polymer electrolyte solution was then used for the fabrication of dye-sensitized solar cell (DSSC).

#### TiO<sub>2</sub> Electrode Preparation and Cell Fabrication

Nanocrystalline TiO<sub>2</sub> semiconductor thin films with an active area of 1 cm<sup>2</sup> were constructed according to the procedure described earlier.<sup>19,20</sup> Dye-sensitized solar cells (DSSCs) were assembled by depositing TiO<sub>2</sub> (P25-Degussa) colloidal paste onto the Fluorine doped tin oxide (F: SnO<sub>2</sub>) photoelectrodes (Fluka) using a simple doctor-blade technique. Here, fluorine doped tin oxide (FTO) glass plate was used as a photoanode and platinum-coated glass plate (Fluka) was used as a photocathode. For the preparation of photoanode, a small amount of TiO<sub>2</sub> colloidal suspension was spread onto the FTO electrodes using doctor-blade method. These electrodes were heated at

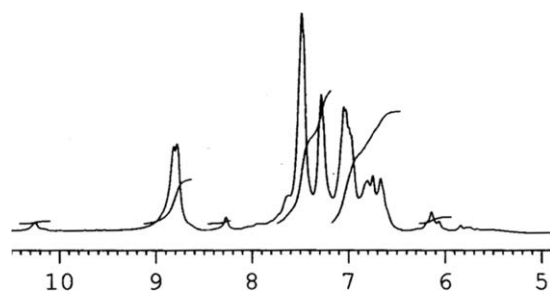


Figure 3. 300 MHz <sup>1</sup>H-NMR spectrum of M-HBPEU(phenylurea terminated) in DMSO-*d*<sub>6</sub>.

**Table I.** GPC, Thermal, and Conducting Properties of Hyperbranched Poly(aryl-ether-urea)

Polymer code	GPC data		Thermal property		Conductivity, $\sigma$ (S/cm)		Relaxation time, $\tau$ (s)	
	$M_w$ (g/mol)	PDI	$T_i$ (°C)	$T_g$ (°C)	Pure polymer	Doped polymer	Pure polymer	Doped polymer
HBPEU	52,400	1.13	276	147	$2.2 \times 10^{-6}$	$8.2 \times 10^{-3}$	$8.51 \times 10^{-7}$	$1.17 \times 10^{-7}$
M-HBPEU	71,120	1.14	276	157	$4.9 \times 10^{-5}$	$4.1 \times 10^{-2}$	$4.79 \times 10^{-5}$	$3.09 \times 10^{-2}$

$T_i$ —decomposition temperature;  $T_g$ —glass transition temperature.

450°C for 30 min, cooled, and then immersed in a  $5 \times 10^{-5}$  M solution of the sensitizer dye—[cis-dithiocyanato-*N,N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)] dihydrate—(N3 dye) in absolute ethanol for 24 h at 25°C and washed again with absolute ethanol and then dried in a moisture-free atmosphere. All such blended polymer electrolyte solutions were directly cast onto dye-adsorbed TiO<sub>2</sub> electrodes. Subsequently, the electrodes were dried and the DSSC assemblies were constructed with the following configuration.

TiO<sub>2</sub>/N3 dye/Polymer electrolyte/Pt.

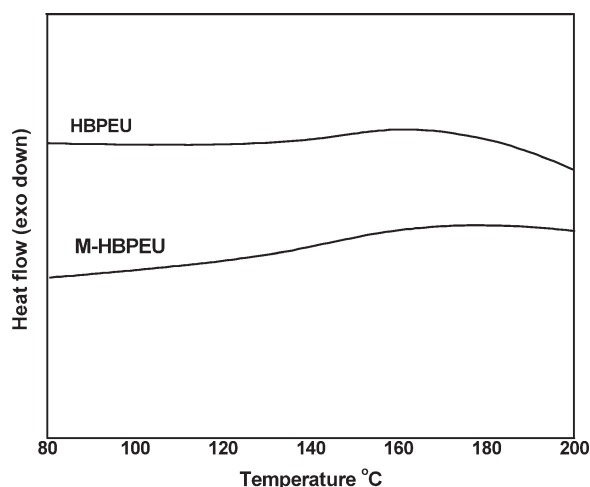
## RESULTS AND DISCUSSION

### Polymer Synthesis

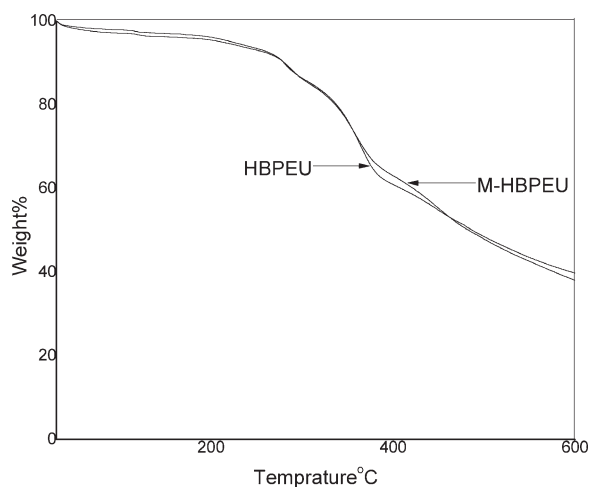
3,5-Bis(4-aminophenoxy)phenyl phenylcarbamate—an AB<sub>2</sub>-type blocked isocyanate monomer containing aryl-ether connectivity—was prepared and solution polymerization of this monomer was prepared according to our previous report.<sup>16</sup> The structures of the polymers were confirmed by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy methods. In the FTIR spectrum of HBPEU, two weak stretching bands were observed at 3300–3400 cm<sup>-1</sup> range due to the free amine end groups present in the polymers. Whereas in the case of M-HBPEU, only one band was observed in the same range and that was very strong and broad due to conversion of free —NH<sub>2</sub> to urea N—H group (Figure 1). Absorption due to the urea C=O appeared at 1682 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectra of amine-terminated HBPEU and end-group modified HBP (M-HBPEU) are given in Figures 2 and 3, respectively, and they exhibited sharp signals for all types

of protons. Protons of free —NH<sub>2</sub> of HBPEU appear as a broad singlet at 5.01 ppm. Both the polymers show three distinct peaks at 10.2, 8.83, and 8.27 ppm; these peaks arise from three different urea NH protons of dendritic, terminal, and linear units of polymers (Scheme 1). In the <sup>1</sup>H-NMR spectrum of M-HBPEU, the peak corresponding to terminal amine protons was completely disappeared at 5.01 ppm and the intensity of peak at 8.83 (urea —NH—) increased proportionally due to reaction of terminal amine with phenyl isocyanate. In the <sup>13</sup>C-NMR spectrum of HBPEU, the carbon substituted with amine was observed at 99.5 ppm whereas this peak was absent in the case of M-HBPEU. These observations unambiguously confirm the structures of polymers.

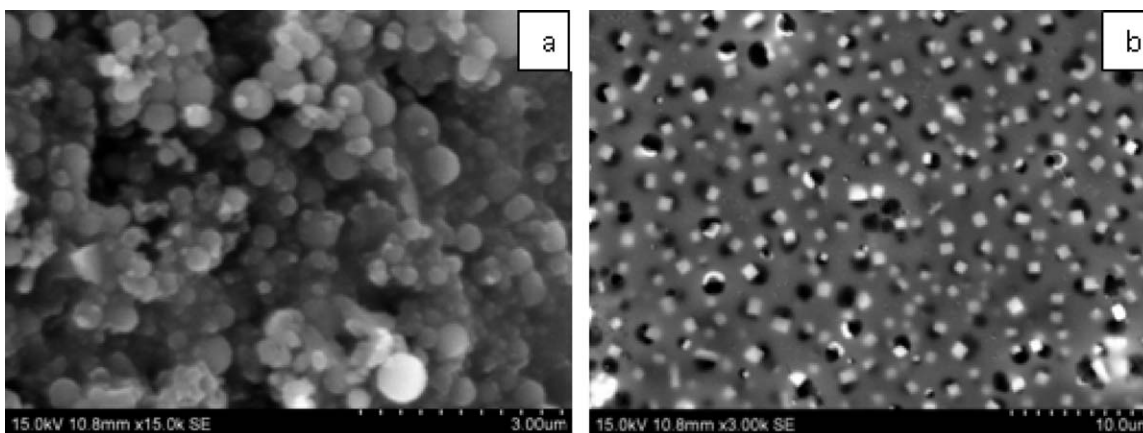
The molecular weight data, thermal stability, glass-transition temperature ( $T_g$ ), and ionic conductivity of both of the polymers are given in Table I. The PDI values of the polymers are narrow due to controlled regeneration of isocyanate functional groups from the blocked isocyanate monomer for polymerization reaction.<sup>21</sup> The molecular weights ( $M_n$  and  $M_w$ ) of M-HBPEU are significantly high compared to HBPEU due to addition of phenyl isocyanate to large number of amine end-functional groups of HBPEU. As this end-group modification increases the phenyl urea hard segment content, the  $T_g$  of M-HBPEU is increased 10°C (Figure 4). However, this end group modification does not alter the thermal stability of the polymer; both the amine-terminated and the amine-modified-into phenyl urea polymers undergo thermal decomposition at identical temperature (Figure 5). The TGA and DSC data given in



**Figure 4.** Second heating differential scanning calorimetry traces of hyperbranched polyurea.



**Figure 5.** TGA thermogram of hyperbranched polyurea.



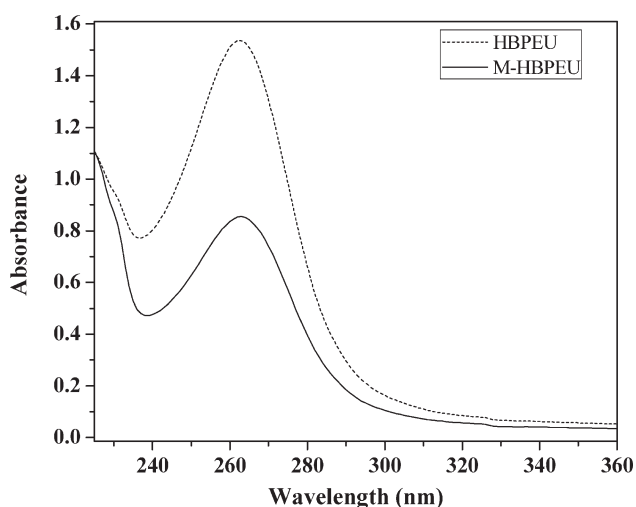
**Figure 6.** SEM image of (a) pure HBPEU and (b) doped HBPEU.

Table I reveal that the polymer chains are flexible substantially below their decomposition temperature.

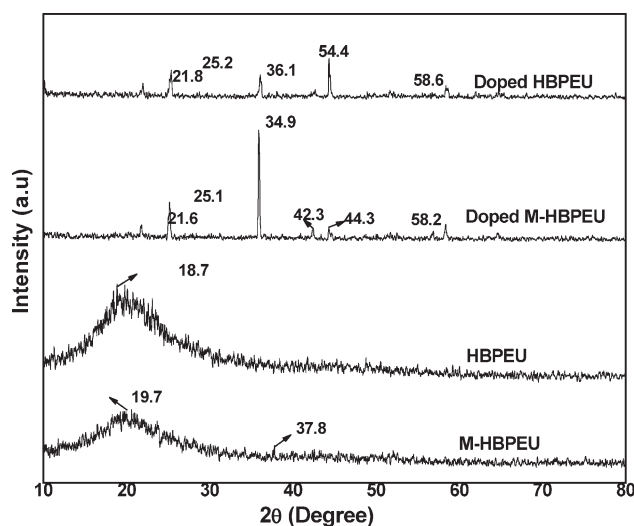
Morphology of pure and doped polymers was examined using SEM and the results obtained were identical for both of the polymers. Typical SEM micrographs of pure HBPEU and doped HBPEU are displayed in Figure 6. Figure 6(a) shows flake-like formation which is a characteristic nature of high molecular weight polymers and these flakes are closely bounded to each other. Whereas in the case of doped polyurea [Figure 6(b)], the morphological feature was completely changed after the addition KI and I<sub>2</sub>. Here, there is a free space between the flakes, and the dopants are uniformly distributed throughout the polymer matrix.

The X-ray diffraction patterns obtained for pure and doped HBPs are given in Figure 7. It is apparent from these X-ray results that the diffraction peaks observed at  $2\theta = 18.7^\circ$  and  $19.7^\circ$  due to crystalline and amorphous spaces present in the pure polymer chains were completely disappeared in the doped polymers. In addition, few new peaks were observed in the doped polyurea complex which indicates that the complexation taken place effectively between pure polyurea, KI and I<sub>2</sub>. As a

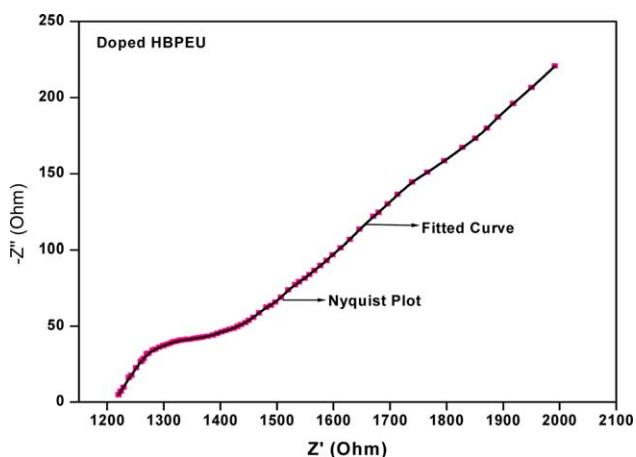
result, structural re-organization had taken place within the doped polyurea containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple which in turn increases the ionic conductivity.



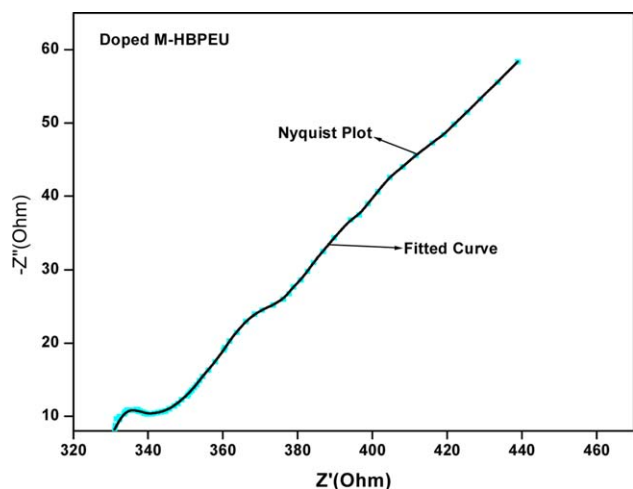
**Figure 8.** UV-Vis spectra of hyperbranched polyurea.



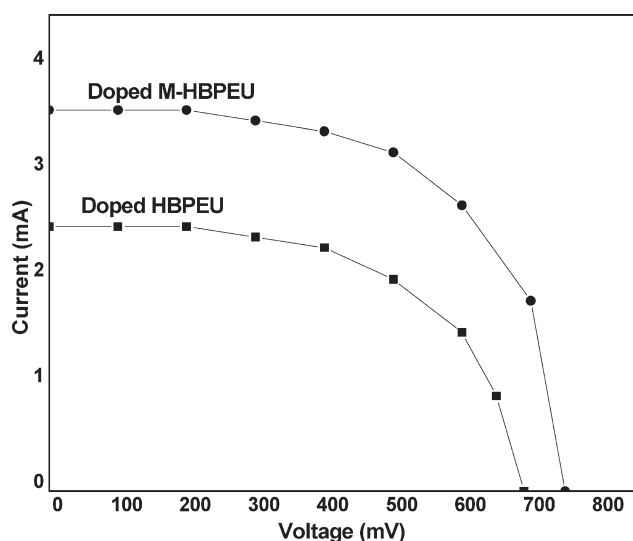
**Figure 7.** X-ray diffraction patterns of pure and doped hyperbranched polyurea.



**Figure 9.** Complex impedance plots obtained for doped HBPEU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** Complex impedance plots obtained for doped M-HBPEU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11.** Current–voltage curve under illumination at 40 mW/cm<sup>2</sup> light intensity.

The globular structure of HBPs influences the electron transporting<sup>22,23</sup> and decreases intermolecular interactions,<sup>24</sup> which are advantages for developing efficient photonic devices.<sup>25</sup> The absorption spectra of HBPEU and M-HBPEU were recorded

and given in Figure 8. Both the polymers shown well resolved absorption at 262 nm without any shift and is due to  $\pi-\pi^*$  transition. This absorption pattern indicates that the modification of end group has no effect on absorption and not affecting the conjugation for electron transport in the polymers.

### Conductivity Measurements

The typical complex impedance plots recorded for both pure and doped hyperbranched polyurea electrolytes are shown in Figures 9 and 10 and the calculated electrical conductivity ( $\sigma$ ) values of the electrolytes are given in Table I. The ionic conductivity of doped polymers was found to be considerably high compared to the pure polymers. Among the two doped polymers, the end-group modified polymer (M-HBPEU) shows very high ionic conductivity of  $4.1 \times 10^{-2}$  S/cm and this range is closer to the conductance of ionic liquids. Moreover, this value is found to be higher than that of doped hyperbranched polyurethanes reported recently for DSSC applications.<sup>14,15</sup> Such a remarkably high conductivity of doped polymer electrolyte conforming that there is effective ion mobility in the aryl-ether-urea skeleton of the polymer chain. The ion mobility is attributed to interaction of metal cations with oxygen atoms in the urea carbonyl groups. Obviously, such interaction will be high in the M-HBPEU in which all the end-groups are phenylurea. The ionic conductivity values, in general, provide information on the mobility of charge carriers within the polymer matrix and influences the photovoltaic performance of the dye-sensitized solar cell (DSSC) in particular by enhancing the  $V_{oc}$  value of the cell.<sup>14,26</sup>

### Current–Voltage ( $I-V$ ) Characterization of the DSSC

DSSCs based on polymer electrolyte are superior over liquid electrolyte-based dye-sensitized solar cells, owing to the stability of the device and the elimination of the use of volatile solvents. For this study, the skeleton of the polymer was designed in such a way that the lone pairs of electrons present in the carbonyl oxygen, ether oxygen, and nitrogen of urea groups readily interact with the metal cations added, which could increase the performance of the DSSCs. The cell operation mechanism has been described in our previous report.<sup>15</sup> The current–voltage characteristics of the photovoltaic cell based on HBPEU/ $I^-/I_3^-/N3$ -dye are presented in Figure 11 and the performance parameters of the cells are summarized in Table II. The cell based on M-HBPEU showed improved performance compared to that based on HBPEU. The low  $V_{oc}$  and  $J_{sc}$  of the cell based on the later polymer electrolyte are due to weak inter-molecular charge transfer (ICT) interaction inside HBPEU and the bad aggregated configuration in solid state which lead to the hindered charge

**Table II.** Performance Parameters of Hyperbranched Poly(aryl-ether-urea) Based N3 Dye-Sensitized Solar Cell

Electrolyte system	Open-circuit voltage, $V_{oc}$ (mV)	Short-circuit current, $J_{sc}$ (mA/cm <sup>2</sup> )	Fill factor (ff)	Efficiency, $\eta$ (%)	Reference
HBPEU + $I^-/I_3^-$	690	2.5	0.55	2.4	This work
M-HBPEU + $I^-/I_3^-$	750	3.6	0.61	4.1	This work
Hyperbranched polyurethanes + $I^-/I_3^-$	755	5.4	0.35	3.5	21
$I^-/I_3^-$	420	1.8	0.44	0.8	27

transport. The enhanced performance including efficiency ( $\eta$ ) of the cell based on M-HBPEU could be explained by strong ICT interaction and better  $\pi$ - $\pi$  stacking of polymer in the solid state. Interestingly, for this case, the fill factor (ff) was found to be 0.61 and an almost steady current of about 3.6 mA was observed up to 500 mV. It is noteworthy to mention here that all the cell parameters corresponding to M-HBPEU were found to be considerably higher than those of our previous work.<sup>14,15</sup> This observation gives an insight into understanding how effectively the end-group modified polymer (M-HBPEU) turned out into a suitable photovoltaic device. The fabricated cell results in a stable device performing under thermal stress maintaining about 70% of its initial value for 2 days in the direct atmosphere without sealing. The experiments were repeated with three such devices and the results were reproduced within an uncertainty of  $\pm 5\%$ . The cell operation mechanism involves absorption of visible light by the chemisorbed dye, and succeeding electron injection from the excited sensitizer into the conduction band of the semiconductor.

## CONCLUSIONS

The use of novel hyperbranched poly(aryl-ether-urea)s as efficient polymer electrolytes along with KI/I<sub>2</sub> as redox carriers in nanocrystalline DSSCs was demonstrated. The XRD results clearly show that the complexation taken place effectively between polyurea and KI/I<sub>2</sub>. The doped polymers had shown remarkably high ionic conductivity compared to pure polymers. The current-voltage ( $I$ - $V$ ) parameters of the doped polymers were found to be higher than those of reported hyperbranched polyurethane. The results indicated that tuning suitably the skeleton of polyurea electrolyte could improve the performance of the solar cell.

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