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Isopropyl alcohol: an unusual, powerful, ‘green’ solvent for the preparation of silicone–urea copolymers with high urea contents

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Abstract

Isopropyl alcohol (IPA) is used as the reaction solvent for the preparation of silicone–urea copolymers. Reactivity of isopropanol with bis(4-isocyanatocyclohexyl)methane (HMDI) was investigated at 23 °C using infrared spectroscopy. Spectroscopic studies indicated very low reactivity of IPA towards HMDI at 23 °C. High molecular weight segmented silicone–urea copolymers were prepared through the reaction of HMDI with aminopropyl and *N*-methylaminopropyl terminated polydimethylsiloxane (PDMS) oligomers and three different chain extenders, ethylene diamine (ED), hexamethylene diamine (HMDA) and 2-methyl-1,5-diaminopentane (Dytek A). Number average molecular weights of PDMS oligomers varied between 900 and 7000 g/mol, respectively. Reactions were carried out at room temperature in IPA. Silicone–urea copolymers with urea hard segment content between 10 and 42% by weight were prepared. Thermal and mechanical characterization of the copolymers indicated the formation of microphase-separated systems with excellent tensile strengths. Interestingly, structure of the diamine chain extender did not show any influence on the mechanical properties of the homologous series of silicone–urea copolymers.

Keywords: Polydimethylsiloxane; Polyurea; Isopropanol

1. Introduction

Silicone–urea copolymers, which are composed of extremely non-polar polydimethylsiloxane (PDMS) soft segments and very polar urea hard segments are very interesting materials. They display unique combination of properties, such as, excellent low temperature flexibility, high UV and oxidative stability, low surface energy, high gas permeability, good electrical, thermal and mechanical properties and physiological inertness or biocompatibility [1,2]. PDMS soft segments, with very low solubility parameters of 15.6 $(J/cm^3)^{1/2}$ or 7.6 $(cal/cm^3)^{1/2}$ show almost complete phase separation from the urea hard segments [3], which have solubility parameters of around 45.6 $(J/cm^3)^{1/2}$ or 22.3 $(cal/cm^3)^{1/2}$ [4]. This leads to very strong hydrogen bonding in the urea hard segments and excellent mechanical properties in silicone–urea copolymers [3,5].

Substantial difference in the polarities of PDMS and urea segments which leads to the formation of high performance elastomers is a major problem from the synthetic point of view, especially if the polymerization reactions are carried out in solution. In order to obtain high molecular weight polymers, the reaction solvent must be a good solvent for the starting materials and also for the copolymer produced [6]. In the preparation of silicone–urea copolymers, especially during the chain extension step where the urea segments are produced, it is very difficult to find a single ‘good’ solvent for the reaction. Tetrahydrofuran (THF) or other ether and diglyme type solvents can be used to obtain high molecular weight silicone–urea copolymers [5,7,8] if no chain extenders are used during the reactions. If a diamine chain extender is used, in order to be able to keep the copolymer in solution it is necessary to use a polar cosolvent. For this purpose highly polar solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAC) and *N*-methylpyrrolidone (NMP) are usually used [2,9]. Although both DMF and NMP are poor solvents for PDMS

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they are useful as cosolvents for the preparation of silicone–urea copolymers with low urea contents. However, at high hard segment contents these solvents are not capable of dissociating the extremely strong hydrogen bonding between urea groups. This leads to the formation of low molecular weight polymers with poor mechanical properties [2,6].

Alcohols are polar solvents which can form strong inter and intramolecular hydrogen bonding. However, since they react with isocyanates to form urethane groups, they are not considered to be good reaction solvents for isocyanate containing reaction systems. Isocyanate–alcohol reactions are second-order reactions. In addition to the reactant concentrations, temperature and catalyst, the rates of isocyanate–alcohols reactions are strongly dependent on the type of isocyanate (aliphatic or aromatic) and the alcohol (primary, secondary or tertiary) [10,11]. Aromatic isocyanates react much faster with alcohols compared with aliphatic isocyanates. Reactivities of alcohols towards isocyanates follows the following order: primary > secondary > tertiary [10]. Although alcohols cannot be used as solvents in the formation of polyurethanes, which require high temperatures and a catalyst, they can effectively be used in the formation of polyureas, especially when the isocyanate is aliphatic in nature. Amines, being much more basic than alcohols, have several order of magnitude higher reactivities towards isocyanates when compared with alcohols [10,12]. Because of this, in many cases polyurea formation reactions are carried out at room temperature or below. This reactivity difference and low reaction temperatures allow the use of secondary or tertiary alcohols as reaction solvents or cosolvents in the preparation of segmented silicone–polyurea copolymers based on aliphatic or cycloaliphatic diisocyanates.

In this investigation we report the reactivity of isopropanol with a cycloaliphatic diisocyanate, bis(4-isocyanatocyclohexyl)methane (HMDI) at room temperature. We also discuss the preparation and characterization of high molecular weight silicone–urea copolymers with high urea contents.

2. Experimental

2.1. Materials

Aminopropyl and *N*-methylaminopropyl terminated polydimethylsiloxane (PDMS) oligomers with number average molecular weights (M_n) ranging from 900 to 7000 g/mol were obtained from Th. Goldschmidt AG, Essen, Germany or from Wacker Silicones, Munich, Germany. HMDI with a purity better than 99.5% was obtained from Bayer, Germany. Reagent grade ethylene diamine (ED), hexamethylene diamine (HMDA), dibutylamine (DBA) and isopropyl alcohol (IPA) were obtained from Riedel de Haen. 2-Methyl-1,5-diaminopentane (Dytek A) was supplied by Du Pont. All reactants and solvents were used as received.

2.2. Kinetic study

Reactivity of HMDI with IPA was investigated by determining the percent conversion of the isocyanate groups into urethane with time by using infrared spectroscopy (FTIR) and isocyanate back titration method [13]. Reaction temperature was 23 °C. During the reactions OH]/[NCO] ratio was kept constant at 20. Since IPA is used as the reaction solvent 20-fold excess is reasonable. During FTIR studies the reaction mixture was introduced into a sealed liquid cell with KBr windows. Path length of the cell was 12 μm. FTIR spectrum of the reaction mixture was obtained at desired time intervals for up to 210 min. Later the sealed cell was placed into an oven at 50 °C, until the complete disappearance of strong isocyanate (N=C=O) stretching peak at 2266 cm^{-1}. Reaction time for this sample is given as infinity (∞). FTIR spectrum of the reaction mixture after 30 min of reaction is reproduced in Fig. 1, which clearly shows all the major peaks used during the kinetic analysis and conversion calculations. These peaks are (i) the antisymmetric and symmetric (C–H) stretching peaks at 2970 and 2933 cm^{-1}, respectively, which were used as reference, (ii) the isocyanate (N=C=O) stretching peak at 2266 cm^{-1} and (iii) the urethane carbonyl (C=O) peak at 1691 cm^{-1}. Percent conversions were calculated by determining the ratios of the absorbance values of the urethane carbonyl peak at 1691 cm^{-1} at different reaction times to that of $t = \infty$.

During the determination of the conversion–time behavior by the isocyanate back titration method the reaction was carried out in a two-neck, round bottom reaction flask, purged with dry nitrogen. Reactor was charged with 5 mmol of HMDI and 200 mmol of IPA. Since HMDI is a difunctional molecule, [OH]/[NCO] ratio was 20 similar to that of FTIR investigation described above. Reaction was followed by removing samples from the

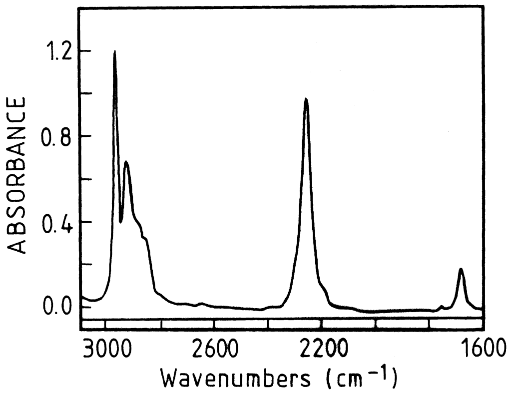

Fig. 1. FTIR spectrum of HMDI/IPA ([NCO]/[OH] = 20) reaction mixture after 30 min of reaction at 23 °C, showing the major peaks used in kinetic calculations.

reactor at desired time intervals, reacting them with excess, standard DBA solution in toluene and back titrating the excess DBA with standard hydrochloric acid solution. Due to very low conversions ($<2.5\%$) within the time frame we were interested in for polymerization reactions (i.e. 30 min or less), we were not able to get reproducible results from titrations. However, after about 60 min of reaction time or above 5% conversions titration results were in very good agreement with the results of FTIR.

2.3. Polymer synthesis

A two-step procedure, known as 'prepolymer method', was used for the preparation of silicone–urea (PSU) copolymers. The first step was the formation of isocyanate-terminated prepolymer, followed by the chain extension with diamines to form high molecular weight copolymers. Reactions were carried out at room temperature (22–23 °C), in a three-neck, round bottom flask, fitted with a nitrogen inlet, stirrer and an addition funnel. A calculated amount of HMDI was introduced into the reactor. Amine terminated PDMS oligomers were weighed in a flask, dissolved in IPA to make about 25% solution by weight and introduced into the addition funnel. Separately, diamine chain extender solutions were also prepared in IPA (25% by weight). Prepolymer was obtained at room temperature by adding the PDMS solution to the HMDI solution in the reactor in approximately 3–5 min. This was followed by the dropwise addition of the chain extender solution through the addition funnel, again at room temperature. The reaction mixture was perfectly homogeneous throughout the reactions and no precipitation was observed. Completion of the reactions was determined by FTIR spectroscopy, following the disappearance of strong isocyanate peak at 2266 cm^{-1}. Total reaction time was usually around 30 min or less. The products obtained were coagulated in isopropanol/water (50/50 by volume) mixture, filtered and dried to constant weight in a vacuum oven at 50 °C.

A similar reaction procedure was used for the preparation of polyether–urea type copolymers in order to also demonstrate the feasibility of IPA as a solvent for polyether based systems.

2.4. Polymer characterization

FTIR spectra were recorded on a Nicolet Impact 400D spectrophotometer with a resolution of 2 cm^{-1}. Intrinsic viscosities were determined using Ubbelohde viscometers, at 25 °C, in IPA. Dynamic mechanical behaviors of the products were obtained on a Seiko Instruments model DMS210 dynamic mechanical analyzer (DMA). Measurements were performed under dry nitrogen atmosphere. The samples were quenched from room temperature to -150 °C using liquid nitrogen and immediately thereafter subjected to a 2 °C/min heating scan at a frequency of 1 Hz. Stress–strain tests were carried out on an Instron Model 4411 Universal Tester, at room temperature, with a crosshead speed of 25 mm/min. For stress–strain tests dog-bone type microtensile test specimens were punched out of thin copolymer films (0.3–0.7 mm in thickness) using a standard die (ASTM D 1708). Stress–strain tests were performed on five specimens for each copolymer sample and average values are reported in Table 3. Films for DMTA and stress–strain tests were prepared by casting from IPA solutions.

3. Results and discussion

Silicone–urea copolymers, which combine extremely flexible and non-polar PDMS chains with highly polar and strong urea groups, display very interesting chemical, physical and mechanical properties [2,3,5]. In spite of their unique combination of properties, preparation of high molecular weight silicone–urea copolymers with high urea contents has been very difficult through solution polymerization. This is mainly due to difficulties in finding the right solvent or solvent combination that will be a good solvent for highly non-polar PDMS but at the same time for highly polar and crystalline urea groups, which can also form extremely strong intermolecular hydrogen bonding [3,4]. The use of polar solvents such as DMF and DMAC as cosolvents in the preparation of silicone–urea copolymers has been demonstrated [9]. However, they were not very effective in producing copolymers with high urea contents. On the other hand high molecular weight silicone–urea copolymers with high urea contents have successfully been prepared through extrusion polymerization [14].

3.1. Reactivity of HMDI with IPA

Alcohols, due to their reactivities towards isocyanate groups are not considered to be potential solvents for urethane formation reactions. However, our preliminary investigations have shown that they are very effective in re-dissolving silicone–urea copolymers prepared in mixed THF/DMF solvent systems. It is also well known that alcohols, especially methanol and ethanol are very effective in breaking up strong ionic and hydrogen bond type interactions in polymeric systems [15]. Although alcohols may not be used as solvents for polyurethane synthesis, we thought they could be potential solvents for the preparation of polyurea systems, where the reaction temperatures are much lower and no catalysts are needed. They can especially be effective when aliphatic diisocyanates are used, since the aliphatic isocyanate/alcohol reactions are several orders of magnitude slower than those of aromatic isocyanate/alcohol reactions [10,12]. Due their lower reactivities towards isocyanates, secondary and tertiary alcohols are expected to be better reaction solvents than primary alcohols.

Taking all these facts into account, IPA, a secondary alcohol seemed to be an appropriate choice as the reaction solvent for the preparation of silicone–urea and polyether–urea copolymers. Stoichiometric balance between difunctional reactants and absence of any side reaction leading to the loss of reactive functional groups are of utmost importance in step-growth polymerization reactions in order to achieve high molecular weight polymers. It is also well established that reactions with monofunctional reactants (such as IPA in this case) are detrimental to chain growth. Therefore, we first investigated the reaction between IPA and HMDI at 23 °C, the reaction temperature for the preparation of segmented urea copolymers. Extent of reaction was determined by two different methods; (i) by FTIR spectroscopy and (ii) by the back titration of isocyanate groups. FTIR spectrum of the reaction mixture after 30 min of reaction is reproduced in Fig. 1, which clearly shows all the major peaks used during the kinetic analysis and conversion calculations. In the FTIR method conversions were determined by comparing the absorbance value of the urethane carbonyl peak at 1691 cm^{-1} at different reaction times to that of $t = \infty$. Antisymmetric and symmetric (C–H) stretching peaks at 2970 and 2933 cm^{-1} were used as reference. Normalized FTIR absorption peaks for the carbonyl region at different reaction times are reproduced in Fig. 2. Results obtained from FTIR studies are summarized in Table 1, which shows the extent of reaction between IPA and HMDI for up to 210 min of reaction. As provided in the fourth column of Table 1, the variation in the ratio of the 2970/2933 reference peaks lies between 1.638 and 1.672. This indicates a total error margin of about 2% or an average error margin of about ± 1% during these studies, which is very good. A time–conversion curve obtained from the FTIR studies for IPA-HMDI reaction is provided in Fig. 3.

Table 1
Conversion–time data obtained from FTIR analysis for the reaction between IPA and HMDI at 23 °C ([OH]/[NCO] = 20)

Time (min)	Absorbance values of selected peaks				Conversion (%)
	2970 cm^{-1}	2933 cm^{-1}	1691 cm^{-1}	2970/2933	
0	1.055	0.632	0	1.669	0
2	1.051	0.636	0.001	1.653	0.11
5	1.052	0.636	0.002	1.654	0.22
10	1.055	0.639	0.008	1.651	0.87
15	1.060	0.646	0.011	1.641	1.19
20	1.053	0.639	0.014	1.648	1.52
30	1.048	0.633	0.023	1.656	2.50
45	1.052	0.629	0.035	1.672	3.80
60	1.047	0.630	0.049	1.662	5.32
75	1.043	0.630	0.060	1.656	6.44
90	1.055	0.644	0.070	1.638	7.60
120	1.053	0.640	0.093	1.645	10.1
150	1.059	0.636	0.116	1.665	12.6
180	1.044	0.637	0.140	1.639	15.2
210	1.050	0.633	0.156	1.659	17.0
∞	1.056	0.639	0.921	1.653	100

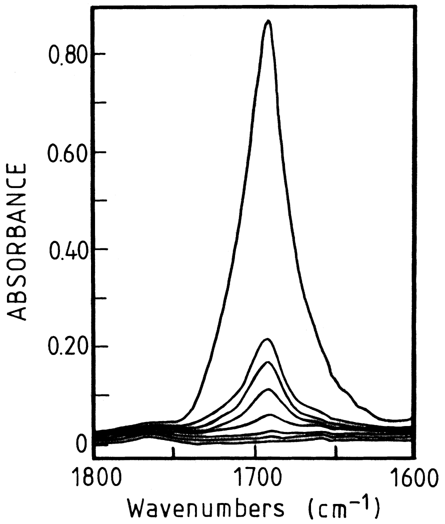

Fig. 2. Development of urethane carbonyl stretching peak at 1691 cm^{-1} as a function of reaction time. Reaction times from bottom to top: 0, 5, 15, 45, 120, 210, 315 and (∞) min.

As explained in the experimental part above, the total reaction time for the preparation of silicone–urea copolymers is usually kept below 30 min. From Table 1 and Fig. 3 it is clear that total consumption of isocyanate groups due to reaction with IPA was only about 2.50% in 30 min. Assuming this as an imbalance in the stoichiometry of the starting materials (i.e. $[\mathrm{NCO}] = 0.975$ and $[\mathrm{NH_2}] = 1.000$) and also assuming 100% conversion during polymerization (i.e. $p = 1.00$), from Carother's equation [16] given below, an average degree of polymerization (X_n) is determined to be 79.

$$X_n = \frac{1+r}{1-r} = \frac{1.000+0.975}{1.000-0.975} = 79 \quad \text{where;}$$

$$r = \frac{[\mathrm{NCO}]}{[\mathrm{NH_2}]} = 0.975$$

Assuming a silicone–urea copolymer based on PDMS oligomer with $M_\mathrm{n} = 2,500$ g/mol and containing 30% hard segment (HMDI + ED) by weight (Sample PSU-2500-30E in Table 2), the average molecular weight of the repeat unit (as shown in the Appendix A) will be 510 g/mol.

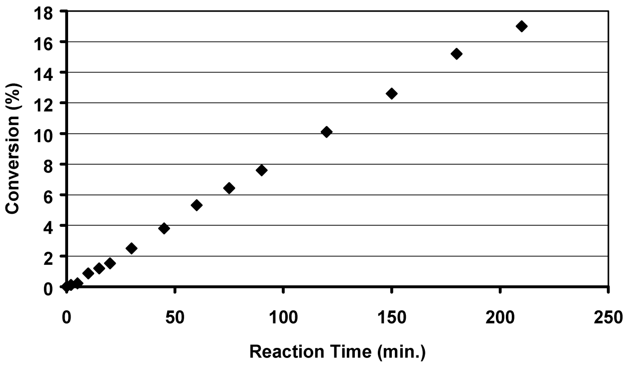

Fig. 3. Conversion–time behavior of HMDI/IPA ([NCO]/[OH] = 20) reaction mixture at 23 °C.

Table 2
Compositional characteristics and intrinsic viscosities of PDMS–urea copolymers obtained from aminopropyl terminated PDMS, HMDI and various diamine chain extenders

Sample code	PDMS M_n (g/mol)	Chain extender	Hard segment content (wt%)	[η] (THF, 23 °C) (dl/g)
PSU-900-30E[a]	900	ED	30	0.48
PSU-900-35E[a]	900	ED	35	0.35
PSU-2500-16E	2500	ED	16	0.24
PSU-2500-23E	2500	ED	23	0.46
PSU-2500-30E	2500	ED	30	–
PSU-2500-17D	2500	DY	17	0.39
PSU-2500-25D	2500	DY	25	
PSU-2500-42D	2500	DY	42	0.33
PSU-2500-20H	2500	HM	20	0.21
PSU-3200-17D	3200	DY	17	0.54
PSU-3200-24D	3200	DY	24	0.40
PSU-3200-30D	3200	DY	30	0.55
PSU-3200-36D	3200	DY	36	0.49
PSU-7000-10E[a]	7000	ED	10	0.50
PSU-7000-18E[a]	7000	ED	18	0.30
PSU-7000-30E[a]	7000	ED	30	–

[a] PDMS is *N*-methylaminopropyl terminated.

Multiplying this by 79 (the average number of repeat units in the backbone) will lead to an average polymer molecular weight of 40,290 g/mol. This is well above the typical molecular weights (20,000–30,000 g/mol) achieved in segmented urea copolymers [17], which are limited by solubility problems. Therefore, we can readily conclude that due to very small isocyanate consumption within typical reaction times, IPA can effectively be used as a polymerization solvent during the synthesis of thermoplastic, segmented urea copolymers based on aliphatic diisocyanates.

In addition to IPA we have also investigated the use of methanol, ethanol and tertiary butyl alcohol as solvents for the preparation of silicone–urea polymers based on aliphatic diisocyanates. Interestingly, alcohols other than IPA, such as methanol, ethanol and *t*-butyl alcohol cannot be used for the preparation of high molecular weight silicone–urea copolymers. PDMS oligomers with number average molecular weights higher than 2,000 g/mol are not soluble in methanol and ethanol. On the other hand *t*-butanol is a good solvent for PDMS but a poor solvent for silicone–urea copolymer at room temperature.

3.2. Polymer synthesis

Following the kinetic studies, which clearly pointed out to the possibility of using IPA as the reaction solvent for silicone–urea systems, copolymers with a wide range of compositions were prepared. Without using IPA as the reaction solvent, it is not possible to synthesize high molecular weight silicone–urea copolymers with high urea contents, especially when ethylene diamine is used as the chain extender. During the preparation of copolymers based on PDMS-2500 or lower, the reaction mixture was completely homogeneous, at every stage, regardless of the hard segment content or structure of the chain extender used. As expected, during every reaction, a drastic increase in the viscosity of the system was observed towards the end of the chain extender addition, clearly indicating the formation of high molecular weight copolymers. During the synthesis of copolymers based on PDMS-7000 with urea contents above 20% by weight, reaction mixtures were homogeneous but translucent.

During this study both primary (aminopropyl) and secondary amine (*N*-methylaminopropyl) terminated PDMS oligomers were used. Average molecular weights of the oligomers were varied between 900 and 7,000 g/mol. Table 2 gives detailed information on the chemical compositions of the silicone–urea copolymers including the type and molecular weight of the PDMS oligomer, hard segment content, the chain extender used and the intrinsic viscosity of the polymer produced. If no chain extenders are used, it is possible to obtain high molecular weight silicone–urea copolymers in ether type solvents [7,8]. However, without using IPA as the reaction solvent it is not possible to prepare high molecular weight silicone–urea copolymers, especially when the chain extender is ethylene diamine [2,18]. As can be seen in Table 2, by using IPA as the reaction solvent it is possible to prepare high molecular weight, ED chain extended silicone–urea copolymers with hard segment contents of up to 40% by weight. Values of the intrinsic viscosities for these samples compare well with silicone–urea copolymers obtained by the reaction of stoichiometric amounts of PDMS and HMDI, containing no chain extender [7,8,14]. Due to the solubility (miscibility) problems encountered during the synthesis reactions, it is very difficult to prepare silicone–urea copolymers based on high molecular weight PDMS oligomers (e.g. $M_n = 7,000$ g/mol) without using IPA as the solvent, especially when diamine chain extenders are employed [7]. As clearly shown in Table 2, by using IPA as the reaction solvent it is possible to prepare high molecular weight silicone–urea copolymers with a wide range of PDMS molecular weights, backbone compositions and fairly high urea hard segment contents.

3.3. Polymer properties

Formation of high molecular weight, high strength silicone–urea copolymers were also confirmed by the results of the tensile tests and dynamic mechanical analysis. Results of the tensile tests on silicone–urea copolymers are provided in Table 3, where the ultimate tensile strength, initial modulus and elongation at break values are provided. As a reference, it is important to note that highly filled and highly cross-linked PDMS elastomers display ultimate tensile strengths of about 10–12 MPa [19]. From data provided in Table 3, it is clear that ultimate tensile strengths of silicone–urea elastomers synthesized during this investigation can be as high as 22.0 MPa. As expected, the ultimate tensile properties of silicone–urea copolymers are mainly determined by two variables, which are; (i) the urea content, and (ii) average molecular weight of the PDMS oligomer. Interestingly, the nature or structure of the chain extender (e.g. ethylene diamine, ED, versus 2-methyl-1,5-diaminopentane, DY) does not seem to have much of an influence on the tensile properties. Due to its compact size and symmetrical structure, intuitively, ED chain extended copolymers are expected to show higher tensile strengths when compared with homologous copolymers chain extended with long and branched DY. Insensitivity of the tensile strength to hard segment structure may be due to very good microphase separation in these systems [2,3]. We have already demonstrated that [5] there is a linear relationship between urea hard segment content and the ultimate tensile strengths of homologous silicone–urea copolymers prepared by the reaction of equimolar amounts of HMDI and PDMS oligomers (M_n; 890–3,750 g/mol) with no chain extender. Interestingly, as shown in Fig. 4, there seems to be a similar relationship for silicone–urea copolymers chain extended with ED or DY. It is also interesting to observe from Table 3 and Fig. 4 that silicone–urea copolymers based on a PDMS molecular weight of 3,200 g/mol show higher tensile strengths than their homologs based on PDMS with average molecular weights of 2,500 or 7,000 g/mol. Investigation is underway in order to better understand the structural, compositional and structural factors leading to such a behavior.

Table 3
Tensile properties of silicone–urea segmented copolymers

Sample code	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PSU-900-30E[a]	140	11.4	290
PSU-900-35E[b]	270	14.5	200
PSU-2500-16E	15.2	5.60	175
PSU-2500-23E	31.0	8.80	110
PSU-2500-30E	42.0	12.0	110
PSU-2500-17D	20.0	6.00	250
PSU-2500-25D	30.0	7.80	130
PSU-2500-42D	120	18.20	90
PSU-2500-20H	19.0	8.10	195
PSU-3200-17D	16.4	9.70	265
PSU-3200-24D	22.0	13.2	205
PSU-3200-30D	34.5	17.9	170
PSU-3200-36D	53.0	22.0	150
PSU-7000-10E	1.2	2.10	420
PSU-7000-18E	2.0	2.65	300
PSU-7000-30E	13.5	7.10	130

[a] Yield point at 12.5% elongation. Yield stress 7.6 MPa.

[b] Yield point at 10% elongation. Yield stress 13.9 MPa.

DMTA analysis also clearly indicates the formation of well-defined, microphase-separated copolymers with excellent thermomechanical properties. Storage modulus-temperature and tan δ-temperature plots for PSU-2500-23-E material are reproduced in Fig. 5, which clearly shows the formation of a thermoplastic material with a sharp PDMS T_g at −120 °C, small PDMS melting peak around −50 °C and a fairly long rubbery plateau extending up to 150 °C. Storage modulus-temperature and tan δ-temperature curves for PSU-7000-18E, which are provided in Fig. 6 also show the formation of a well phase separated elastomer with a PDMS T_g at 120 °C, followed by a sharp PDMS melting around −50 °C and an unusually flat and long rubbery plateau extending up to 160 °C, covering a temperature range of about 200 °C.

4. Conclusions

It has been demonstrated that IPA is a powerful, ‘green’ reaction solvent that can be used for the preparation of high molecular weight, high strength silicone–urea copolymers based on a cycloaliphatic diisocyanate (HMDI). By using IPA as the reaction solvent it is possible to prepare silicone–urea copolymers with very high urea hard segment contents and ultimate tensile strengths above 20 MPa. Interestingly, alcohols other than IPA, such as methanol, ethanol and

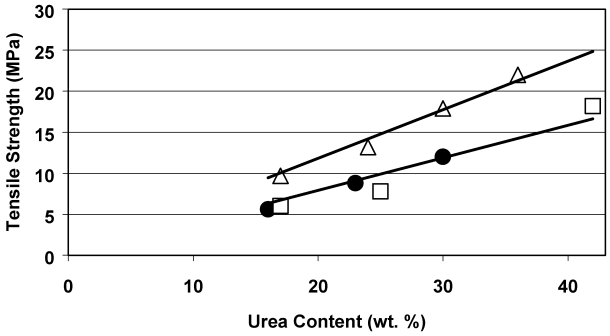

Fig. 4. Ultimate tensile strengths of siloxane–urea copolymers as a function of urea hard segment content and PDMS segment length. (●) PSU-2500-E series, (□) PSU-2500-D series, and (△) PSU-3200-D series.

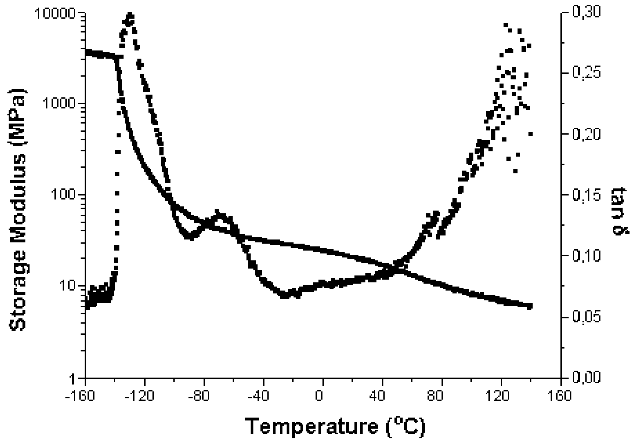

Fig. 5. Modulus-temperature and tan δ-temperature behavior of PSU-2500-23E.

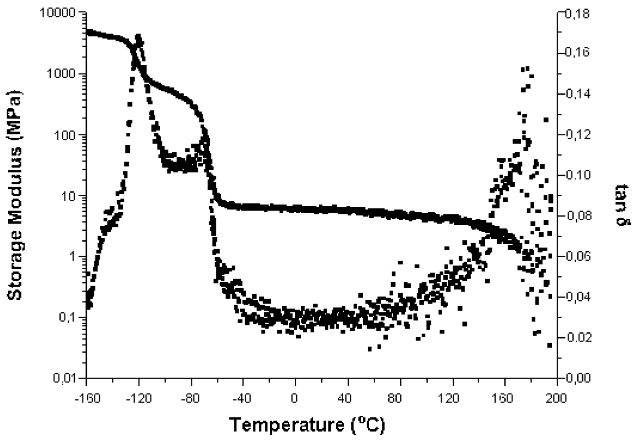

Fig. 6. Modulus-temperature and tan δ-temperature behavior of PSU-7000-18E.

t-butyl alcohol cannot be used for the preparation of high molecular weight silicone–urea copolymers since PDMS oligomers with number average molecular weights higher than 2,000 g/mol are not soluble in methanol and ethanol. On the other hand *t*-butanol is a good solvent for PDMS but a poor solvent for silicone–urea copolymer. By using IPA as the reaction solvent, we have demonstrated that it is also possible to prepare high molecular weight, segmented polyether–urea elastomers based on amine terminated poly(ethylene oxide) and poly(propylene oxide) oligomers. A manuscript describing the synthesis and properties of polyether–urea copolymers will be forthcoming.

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Appendix A

Calculation of the number average molecular weight of the repeat unit for the segmented silicone urea sample PSU-2500-30E given in Table 2.

Chemical composition of PSU-2500-30E, which is based on PDMS-2500 and contains 30% (by weight) of urea hard segment (HMDI + ED) is as follows:

PDMS-2500	70.0 g	28 mmol
HMDI	25.7 g	98 mmol
ED	4.2 g	70 mmol

$$M_n = (28 \times 2500 + 98 \times 262.35 + 70 \times 60.12)/(28 + 98 + 70) = 510 \text{ g/mol}$$

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