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Organo-gelation using Microwave Heating Source: The Case of a Polyurethane Model Compound

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Abstract

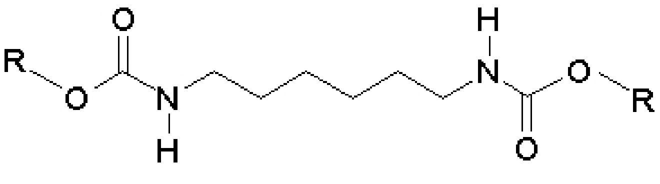
Organo-gels with a series of biscarbamates as gelators were prepared using microwave (MW) heating source as well as conventional heating. Biscarbamates with alkyl side chain lengths varying from C_5 to C_{18} were used, with six solvents having dipole moments ranging from 0.07 to 4.3 D. The minimum gelation concentration and the time required for dissolution were significantly reduced with MW heating with benzonitrile, compared to the conventional heating for all the side chain lengths of the biscarbamates. While such reduction was pronounced with benzonitrile and dimethyl sulfoxide with large dipole moments, the time required for dissolution increased with MW heating (compared to the conventional) in the case of xylene and toluene with small dipole moments. Thus, MW is effective with solvents possessing large dipole moments. Although the gels consist of fibers using both methods, an inherent orientation of these fibers was seen with MW heating.

Keywords: Gelators; Monomers; Organo-gelation

Introduction

Non-conventional techniques such as microwave (MW) as the heat source, ionic liquids as an alternate medium, ultrasound, and ball-milling have been explored in the past few years for synthesis and processing of materials. A tutorial review on these methods has been presented recently by Vázquez [1]. Microwave-assisted organic synthesis was first demonstrated in the research labs of Giguere [2] and Gedye [3]. It was shown that the use of microwave dramatically accelerated the rate of many organic reactions compared to conventional conductive heat. This technique recognizes the ability of some materials to transform electromagnetic energy into heat. Since then, microwave heating has been applied not only to reduce reaction time [2-5] but also to improve yields [6,7] and selectivity in non-solvent [8,9]. The process also allows reactions to occur with limited or absence of catalytic reagents which has great benefits in the field of synthetic chemistry. We have shown that in the case of curing of polymerizable monomers to fabricate a polyimide resins, the time to completion of curing was reduced to an hour, compared to more than 30 hrs using the conventional heating [10]. Nüchter [11] combined MW and mechano-chemistry for conducting organic reactions. Recently, Dudley [12] and Stiegman [13] presented a detailed discussion on the effect of the dipole moment of the solvent and solute and other parameters that affect the MW heating.

We have previously reported the organo-gelation with biscarbamates (Scheme 1), which are model compounds for polyurethanes [14-16]. These are self-assembling molecules, with two hydrogen bonding motifs separated by a $(CH_2)_6$ alkyl spacer. Preparing the gels usually involves selecting a liquid that is a non-solvent for the molecule (gelator) at room temperature, but would dissolve upon heating to a higher temperature. Cooling the solution leads to the self-assembly of the molecule in the presence of the solvent, with predominant growth along the hydrogen bonding direction [14]. Such directional growth results in fibers which trap the solvent molecules and gelation occur. A minimum concentration of the gelator is required for gelation. In addition, the phenomenon also depends on the solute-solvent pair. In the absence of gelation, crystallization and precipitation would occur. While several studies on MW assisted synthesis and processing have been reported in the literature as mentioned above, we examined the effect of MW heating method on organo-gelation using the biscarbamates, with alkyl chain length ranging from C_5 to C_{18}. Six solvents with different dipole moments were used. The minimum concentration (C_{min}) of biscarbamate required for gelation, the dissolution and the gel-to-solution temperatures, as well as the morphology of the gels was determined using MW and conventional heating.



Scheme 1: Biscarbamate with a C_6 spacer between the hydrogen bonding groups. R is an alkyl side chain of length varying from C_3 to C_{18}.

Experimental

The synthesis of biscarbamates with different alkyl side chain lengths was described before [14-17]. This involves reacting 1,6-diisocyanatohexane (0.1 mol) with various alcohols (0.2 mol) ranging from 1-propanol to 1-octadecanol in presence of a catalyst 1,4–diazabicyclo [2,2,2] octane (DABCO). As in our previous publications, we designate the biscarbamates as C_x where x denotes the number of carbon atoms in the alkyl side chains.

Preparation of the gels and xerogels

As with our previous work, benzonitrile was used primarily.

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Gels of concentration 0.08 M were prepared in capped vials to avoid evaporation of the solvent. Gels were also prepared with DMSO, 1-octanol, xylene, toluene, and dodecane to study the effect of the solvent type. Conventional hot plate as well as the microwave source were used for preparation of the gels. For the gels prepared using the hot plate, weighed amounts of biscarbamates of different alkyl side chain lengths were dissolved in requisite amount of solvent in an oil bath at around 80-100°C, which is about 20°C above the dissolution temperature, resulting in clear solutions. This would ensure that the solution would be free of any remaining nuclei which would promote gelation through a self-seeding process. Gels were made by slowly cooling to room temperature by turning off the hot plate. Tube inversion was used as a "quick check" for the gelation. The norm that is usually used is that when the vials were turned upside down, if the solute/solvent were not visually separated and did not flow they were considered as gels.

For the gels prepared using the microwave system, weighed amounts of biscarbamates of different alkyl side chain lengths and the requisite amount of solvent were placed in a 20 ml Pyrex vial. The vial was then placed in a porcelain vessel into an ETHOS PRO microwave digestive system running with the Milestone Digestion operating system. The samples were exposed to a maximum power of 1000 W of radiation as the software automatically delivers the minimum power required to follow the defined temperature profiles. The chamber containing the samples was programmed to set temperatures ranging from 40 to 160°C in 10 minutes and to keep that temperature for 30 minutes to two hours. The temperature of the chamber was measured using a temperature probe (ATC-400) inserted inside a reference vessel. This allows for the monitoring of the thermal conditions and adjusting the microwave parameters to achieve the desired temperature profile inside all the vessels. As the concentration and the solvents changed, the program temperature was modified to ascertain that the fully dissolved solutions were obtained prior to lowering the temperature for gelation. Due to visual limitations of the instrument, we were not able to determine the dissolution temperature visually. At the end of the entire heating and cooling process, the vials that do produce a uniform gel were considered to have an adequate dissolution temperature, while the samples which show precipitation or partial dissolution are determined to have insufficient heating. The radiation was then terminated and the samples were left to cool to room temperature at a rate of 1°C/minute for an hour. Once again, the vials were turned upside down to check for gelation. All the gels were opaque. These gels were dried at room temperature for a day and then kept under vacuum for a few days to form xerogels. There were no signs of degradation or chemical reactions of the biscarbamate molecules when using microwave heating.

Characterization

Thermal analysis was performed using a TA Instruments 2010 differential scanning calorimeter at a heating rate of 10°C per minute. This method allows for the measurement of the melting temperature of the gels: also known as the gel-to-solution temperature ($T_{gel\text{-}sol}$). Differential scanning calorimetry also allows us to determine the formation of the gel i.e., the gelation temperature (T_{gel}). However, since the technique requires the sample to be heated in a conventional manner, acquiring T_{gel} for the microwave gels is not possible. The calorimeter was calibrated for temperature and energy with an indium sample as a standard reference material. Sample preparation for the wet gels involved putting 30 mg of the wet sample in aluminium pan (50 μL) without the lid and let the sample sit in the fume hood for 10 minutes. The lid was then crimped to the pan while making sure no solvent or condensation would escape. Since the maximum temperature used for the DSC scans did not exceed 100°C, deformation of the pan due to excess vapors would not alter our results. The difference in the recording temperature was less than 1°C. The software TA Instruments Universal Analysis 2000 (version 3.9A) was used to analyze the thermographs.

Optical micrographs (OM) of the gels were recorded using a Zeiss Axioplan polarized optical microscope (POM) along with the Northern Eclipse (version 8.0) image-processing software. SEM images of the xerogels were obtained using a JEOL JSM-6400 scanning electron microscope. They are then mounted on carbon tape and sputter coated with 80: 20 Au/Pd alloy. SEM images were captured at an accelerating voltage ranging from 5 to 20 kV. Vega TC software were used for the microscope manipulation and capturing the images.

Results and Discussion

Gelation with the biscarbamates involves the self-assembly enabled by two hydrogen bonding sites and van der Waals interactions between the alkyl side chains in solution. As discussed before, with an increase in the length of the alkyl chain, the relative contribution from van der Waals interactions is enhanced whereas the number of hydrogen bonds remains the same [18]. Generally for these biscarbamate gels, as the length of the alkyl side chain increases, the minimum concentration required for gelation (C_{min}) decreases (Figure 1) since the van der Waals interaction increases with the chain length [14]. Abdallah and Weiss [19] found a similar trend in the case of n-alkanes.

Figure 1 shows that microwave heating yields gels with lower C_{min} even for gelators with short alkyl chains. For the gels made using the hot plate, the minimum concentration for the biscarbamate with the short C_6 side chain is 0.08 M with benzonitrile whereas it is 0.06 M for the gel produced using microwave heating. The reduction in the C_{min} is significant with C_7 to C_{10} side chains. Typically, with conventional heat source, biscarbamates with side chains shorter than C_6 do not produce gels even at high concentrations; they would precipitate. However, with microwave heating, we were able to produce a gel with biscarbamate with the even shorter C_5 side chain, at a concentration of 0.096 M. As of now, C_5 is the shortest biscarbamate that can produce a gel using microwave radiation [20].

In previous reports on microwave chemistry, yields of certain organic reactions have significantly increased while the use of catalyst

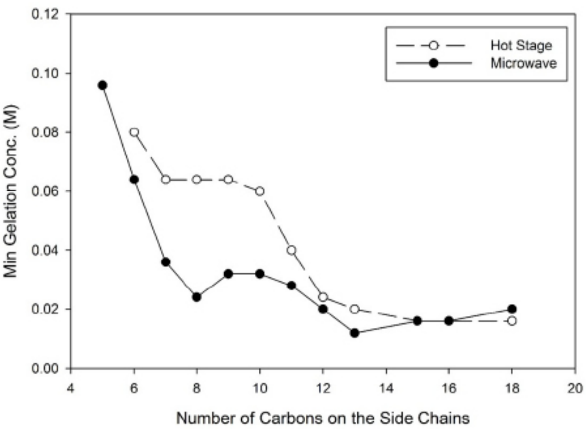

Figure 1: Change in the minimum gelation concentration as a function of number of carbon atoms in the alkyl side chains using the hot plate and the microwave system.

have remained the same or decreased [21,22]. Certain early reports described rate accelerations of several orders of magnitude over conventional heating, leading to speculation that non-thermal coupling of microwave radiation with molecules in solution can alter or reduce the activation energy of the reaction [12]. This may also be similar to lowering the critical gelation energy required to produce these gels.

Figure 2 shows the variation of the dissolution temperature (T_{diss}) with alkyl side chain length for the gels made using MW and conventional heating. This temperature relates to the temperature required to dissolve the gelator and produce the gel. We previously observed an increase in the temperature with the length of C_n side chains, where *n* was even [14]. Although the trend is similar in the present work with both even and odd numbered C_n side chains, we observe an odd-even effect, with the T_{diss} of an odd C_n being higher than that of succeeding even C_n. We observed a similar odd-even effect in our previous study on the effect of carbon atom parity on the crystalline melting temperature (T_m) and spherulites size of these biscarbamates [23]. Those with odd C_n side chains showed a higher T_m and larger spherulites size. We rationalized it on the basis of the *syn* and *anti-* conformations of the end groups with respect to the closest ester oxygen. The inherent differences in the molecular structure would lead to different packing modes for the odd and even series. We speculate that biscarbamates with odd C_n side chains are more densely packed due to the hydrogen bonding in accordance with dispersion forces. As T_{diss} is related to T_m, we observe the same variation in temperature.

Figure 2 shows that the T_{diss} of the biscarbamate gels with benzonitrile produced using the MW source to be significantly lower than those of the gels prepared with the hot plate. While the difference in T_{diss} is about 8-12°C with C_6, C_7 and C_8 biscarbamates, it is 14-25°C with longer side chains. This can be attributed to the manner in which the energy gets distributed in the system. The conversion of microwave energy into thermal energy requires a medium that interacts with and absorbs microwave electromagnetic radiation in such a way that heat is generated [24]. This phenomenon is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. The electric component of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction [25-27]. Irradiation of the sample at microwave frequencies results in the molecular dipoles aligning with the applied electric field. As the dipoles rotate and align themselves energy is dissipated in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. For the homogeneous biscarbamate solutions in benzonitrile, such loss processes occur uniformly throughout the system, enabling the rapid and efficient volumetric heating so the solution to gel temperature is generally lower.

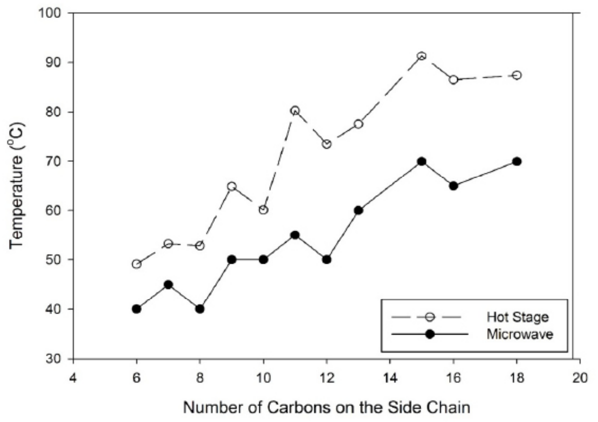

Figure 2: Change in the dissolution temperature of the 0.08 M biscarbamate gel in benzonitrile made using a hotplate or a microwave system as a function of number of carbon atoms in the alkyl side chains.

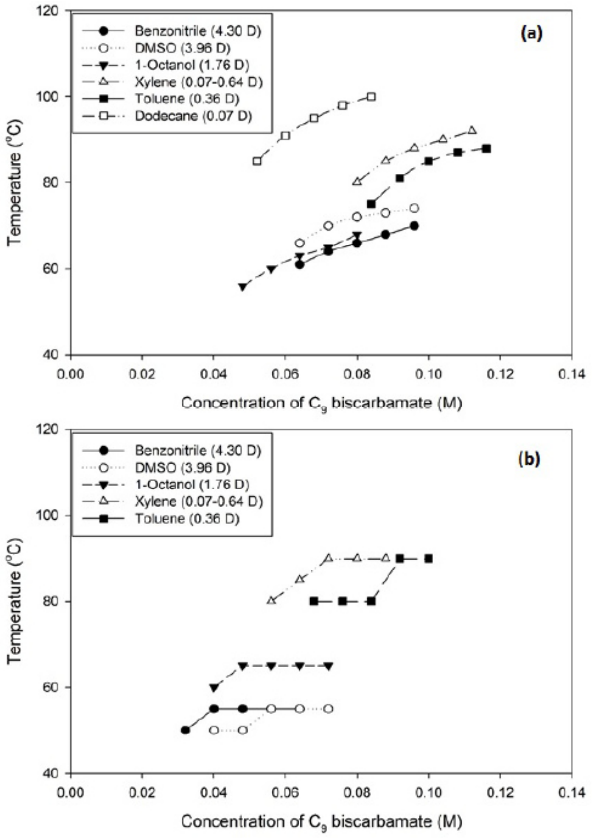

Figure 3: Minimum dissolution temperature for C_9 biscarbamate gels in various solvents using (a) conventional and (b) microwave heating, for a range of gelator concentrations starting with the critical gelation concentration. The dipole moments of the solvents are listed in the insets.

Apart from benzonitrile, in a previous study, we were able to form biscarbamate based gels with other solvents such as 1-octanol, xylene, toluene or dodecane using the conventional heating method [14]. We attempted to prepare gels with these solvents and C_9 biscarbamate using microwave heating. Figure 3 shows the T_{diss} of the gels from different solvents for a range of gelator concentrations (starting from the minimum gelation concentration for each of the solvents), using the conventional and microwave heating methods. The dipole moments of the solvents are listed in the insets and these range from 0.07 D for dodecane to 4.3 D for benzonitrile. There are some clear differences arising with the two heating methods. When conventional heating was used (Figure 3a), the T_{diss} ranged from 55 to 70°C for the three solvents benzonitrile, 1-octanol and DMSO, with the former two exhibiting the lowest temperature. The gelation of the other three solvents required a much higher temperature range. When MW heating was used (Figure 3b), the T_{diss} recorded were found to be similar to those for the conventional heating method with the exception of dodecane where a gel was never produced and the samples yielded only precipitated solutions. However, the amount of heating time varied significantly depending on the solvents. For benzonitrile and DMSO, the microwave ramps up to the desired temperature and is heated for 30 minutes until the machine cools down which allows for the gel to set. For 1-octanol, the sample required an additional hour of MW heating to fully dissolve, and the samples in toluene and xylene required a total of two (2) hours of MW heating. These differences in the amount of heating illustrate the impact of the solvent use in the microwave. It does appear that solvents with a higher dipole moment require less heating to fully dissolve. The three distinct ranges correspond to (i) benzonitrile and DMSO which have a dipole moment of 4.3 and 3.96 D respectively, showing the lowest T_{diss} and requiring the least amount of time (ii) 1-octanol with a smaller dipole moment of 1.76 D, requiring more heating than benzonitrile and DMSO and (iii) xylene and toluene with much smaller dipole moments requiring even more heating. Thus a clear trend is seen with the dipole moment of the solvents and the effectiveness of MW heating.

Interestingly, it is seen from Figure 3 that for all the solvents, the gels that were prepared using MW heating required a lower C_{min} than those obtained from conventional heating. For example, with benzonitrile, the minimum concentration required to form gels is 0.065 M with conventional heating, and it decreased to 0.03 M with MW heating. Similar is the case with DMSO, for which C_{min} decreased from 0.065 M to 0.04 M. There is a decrease of at least 0.01 M in C_{min} for the other solvents These results illustrate that the nature of solvent has an effect for specifically microwave heating. As for the gelator, the C_9 biscarbamate has a dipole moment of 0.10D (as calculated from a geometrical optimization at PM3 level of theory using HyperChem and Spartan ES software), and the bond moment of the C = O bond is 2.3 D. As discussed above, the conversion of microwave energy into thermal energy requires the solvent medium or the reagents to absorb microwave energy and convert it into heat. Solvents such as toluene and xylene with lower dipole moment do not produce enough heating for the dissolution of biscarbamate. In fact, it was observed that in increase in heating was required to dissolve these samples.

The fibrous morphology of the gels prepared with MW heating is similar to those made with conventional heating. Figure 4 shows the OM (wet gels) and SEM (xerogels), of the gels prepared by the two methods, with C_9 biscarbamate and benzonitrile. There is no significant difference in the length and width of the fibers of the gels prepared by the two heating methods. Interestingly however, gels produced under microwave radiation show bundles of fibers aligned in one direction whereas this orientation is absent for gels produced using conventional heating. Such orientation of fibers was seen consistently and is not fortuitous or an artifact. We had previously prepared aligned fibers of benzonitrile/ biscarbamate gels by using a magnetic stirrer while the solution was being cooled [14]. However, in the case of Figure 4 there was no magnetic stirrer involved. This might indicate that the radiation has an effect on the self-assembly of the biscarbamate molecules by reorienting and aligning the biscarbamate molecules which promotes hydrogen bonding and van der Waals interactions along a direction.

We compare the gel-to-solution temperatures ($T_{gel\text{-}sol}$) for the gels obtained using conventional and microwave heating methods (Table 1). The differences in $T_{gel\text{-}sol}$ vary depending on the solvent used; this is dependent on the gel strength in the solvents. Interestingly, despite the differences in dissolution temperatures for the production of the gels, $T_{gel\text{-}sol}$ are very similar in value. This indicates that both heating methods produce gels with similar physical properties. The fact that the morphology of these gels in benzonitrile and DMSO also show similarities further illustrates that both heating methods yield comparable gels. The main differences between both techniques are the critical gelation concentration and the temperature required to dissolve the initial components. From these finding, we were also able to assess the gelation temperature (T_{gel}) for the microwave gels as we were unable to determine them experimentally. Considering how alike $T_{gel\text{-}sol}$ are for both methods, we can infer that the T_{gel} will be in the same range as for the gels produced using conventional heating.

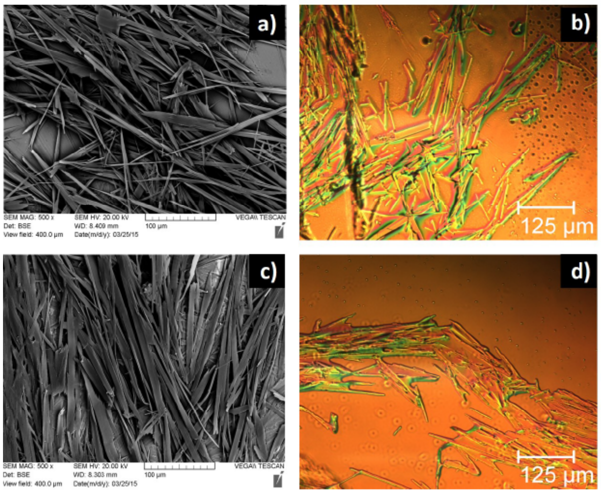

Figure 4: (a) SEM and (b) OM images of benzonitrile/ C_9 based gels using conventional heating. (c) SEM and (d) OM images of gels made using MW source.

	Conventional Heating		Microwave
Solvents	**$T_{gel\text{-}sol}$ (°C)**	**T_{gel} (°C)**	**$T_{gel\text{-}sol}$ (°C)**
Benzonitrile	64.6	59.0	65.4
DMSO	82.2	63.1	81.8
1-Octanol	59.7	33.5	56.2
Xylene	69.3	58.8	69.6
Toluene	65.5	56.5	66.9
Dodecanol	86.3	59.4	N.A.

Table 1: The gel-to-solution temperatures for gels produced using conventional heating and microwave heating methods, and the gelation temperature for the conventional heated gels. Due to limitation of the microwave apparatus, the gelation temperature cannot be determined for this method.

Conclusions

In conclusion, we have shown that microwave radiation could be used to prepare organo-gels of biscarbamates. With benzonitrile as the solvent, for biscarbamates with various alkyl side chain lengths, both the minimum concentration (C_{min}) required for gelation and the temperature required to produce the gel decreased with MW heating compared to the conventional. Gels prepared with different solvents show that the dipole moment of the solvent plays a role in these properties when MW is used. Solvents such as benzonitrile and DMSO are more effective in this regard than xylene or toluene. In addition, it was possible to prepare gels with the biscarbamate with a short alkyl side chain using MW, while it was not with conventional heating. Irrespective of the different opinions in the literature on the effectiveness of MW radiation in chemical processes, the differences that we observed between the conventional and MW heating methods do point to the merit of the latter. From the perspective of scientific novelty we have demonstrated that the latter has the advantage of reducing the gel forming temperature and the concentration required.

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