Telechelic Siloxanes with Hydrogen-Bonded Polymerizable End-Groups. II. IR Studies of End-Groups Interactions—Model Amides and Ureas

M. Mazurek, C. M. Leir, R. K. Galkiewicz

3M Display and Graphics Business Laboratory, 3M Center, St. Paul, Minnesota, 55144

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ABSTRACT: Hydrogen-bonding phenomena in amides and ureas are of great practical and theoretical importance. In this article, we report on infrared temperature studies aimed at the elucidation of the hydrogen-bonding phenomena of (meth)acrylamide groups directly linked to the alkyl groups of telechelic polydimethylsiloxane (PDMS) which serve as models of monoamides, or linked to the alkyl groups of telechelic PDMS through amide spacers-models of diamides (dipeptides). Similarly, we have examined the hydrogen-bonding phenomena in urea-terminated telechelic PDMSs to which free-radically polymerizable groups (methacrylate, α-methylstyryl) are attached. Hydrogen bonding in the derivatives of these substituted silicone amides and ureas in the unreacted (liquid) state has been studied, as well as in films formed via ultraviolet-initiated free-radical polymerization of those reactive end-groups. The extreme flexibility of the silicones provides a medium in which polar, hydrogen-bonding end-groups (amides, diamides, and ureas) phase-separate to form their own domains wherein they can freely aggregate in an essentially unperturbed state, when in the liquid form. When the vinyl end-groups are polymerized, interactions between the hydrogen bonding groups attached to them can be studied in a spatially constrained environment. High thermal stability of the silicones allows the study of the hydrogen bonding (H-bonding) phenomena of these models within a broad temperature range. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 982–995, 2010

Key words: copolymerization; curing of polymers; FT-IR; functionalization of polymers; polysiloxanes

INTRODUCTION

In the previous paper in this series,[1] we presented the results of our study of the physical properties of a family of curable telechelic polydimethylsiloxanes (PDMS) "liquid rubbers" and of crosslinked elastomers obtained upon the UV initiated polymerization of their free-radically reactive vinyl end-groups. These liquid intermediates, ranging in molecular weight from 5000 (5k) to 50,000 g/mol (50k), were readily prepared from high purity primary amine-terminated silicones by treating them with various acylating agents and isocyanates to provide a series of carboxamide- and urea-functionalized reactive oligomers. In spite of the low nominal concentration of the reactive end-groups (~ 5 wt % to 0.5 wt % depending on PDMS molecular weight), the curing of these materials was fast and efficient, with virtually all chains becoming incorporated into the final crosslinked network. These results were attributed to the fact that the highly polar amide and urea terminal groups are incompatible with the low-polarity PDMS medium and they separate into discrete phases, making effective high local concentration of the reactive groups attached to them.

As a consequence of this association of end-groups into separate domains, the individual PDMS chains become reversibly linked together into a liquid transient network. This linking is reflected in an increase in the viscosity of the silicone fluids upon functionalization. Depending upon the particular end-group, the viscosity increase ranged from slight [Acrylamido-functional siloxanes (ACMS)] to dramatic [Acrylamidoamido-functional (ACMAS) and α-Methylstyrylurea-functional siloxanes (MeStUS)]. These viscosity differences were thought to be, in addition to polar interactions, a reflection of the strength of the H-bonding that occurs between the various amide and urea end-groups. Thus, the viscosity of the acrylamidoamido compound (5k ACMAS) is much higher than the corresponding methacrylamidoamido derivative (5k MACMAS). Likewise, the viscosity of the methylstyrylurea terminated silicone (5k MeStUS) was surprisingly much higher than that of the methacryloxy urea (5k MAUS).

The primary aim of this second paper is to help better understand the role hydrogen bonding plays

Correspondence to: M. Mazurek (mhmazurek2@mmm.com).

within these materials, and to illustrate that these types of materials might serve as models to further studies of H-bonding phenomena in amides, diamides, and ureas. We hope that others might agree and, as a result, perform much more in-depth analyses of systems and materials like these, which for us have primarily been of strong practical importance.[2]

Telechelic silicones appear to provide an ideal medium for model studies of the nature of hydrogen bonding in amides, diamides, and ureas, and other H-bonding groups by IR spectroscopy. In fact, one can imagine extending this approach to a more elaborate species, such as, oligopeptides. The polar amide, diamide, (dipeptide) or urea groups, while chemically attached to both ends of polysiloxane chains, tend to form their own domains as they are inherently immiscible with nonpolar silicones. These amide or urea end groups can freely assemble, by virtue of H-bonding forces, into small aggregates which are restricted by the morphology of the transient network from growing beyond a limited size, thus preventing crystallization phenomena notorious in low molecular weight amides or ureas. This size limitation also prevents the macromolecules formed in the process of polymerization (oligomerization) of the vinyl end-groups from organizing into macroscopic crystalline solids, characteristic of many polyamides, and some polyureas. The extreme flexibility and high thermal stability of the silicones allow the examination of the effect of temperature on the H-bonded amide, diamide or urea groups in an essentially unperturbed state. If it is assumed that the characteristic infrared bands are unequivocally assigned—and the body of the data available in the literature, at least for model amides is overwhelming—then these model polymers allow, at least in principle, a study of the H-bonding patterns, conformational ordering, and changes in packing of the H-bonding groups. Importantly, additional information can be obtained from a comparison of data concerning these essentially unperturbed interactions between amide or urea groups in the model liquids with the results of an analysis of the spectra of the networks formed by free-radical oligomerization of these telechelic siloxanes. In these cases, the hydrogen-bonding groups are attached as regularly spaced (at every other carbon) substituents on the polyvinyl chain, which obviously imparts some structural and conformational constraints on the H-bonding groups. The other benefit of using siloxane functional fluids is that the amide or urea groups studied are immersed in a strongly hydrophobic medium, which minimizes the effect of water on the spectra—a major problem, most prominently reflected in the N—H stretching band.[3]

Controversies continue regarding not only a quantitative interpretation of the temperature dependence of IR spectra but also regarding signals assignments within polyamides,[3–6] and to a lesser extent to polyureas and polyurethanes,[7] as we discuss immediately below. However, it is not our aim to contribute to those controversies, but instead, we hope that the polymers described in this article will provide some feasible path to additional models for studying hydrogen bonding phenomena in an idealized environment.

HYDROGEN BONDING IN AMIDES

The elucidation of the nature of hydrogen bonds in polyamides is of great theoretical and practical interest, and as such it has been a subject of extensive studies over the last several decades. Early on, it was recognized that vibrational spectroscopy could be used as an effective tool to discriminate between various associating species.[4,8] The significance of understanding of H-bonding in amides primarily stems from the role of the amide group in biological macromolecules, e.g., H-bonding plays an essential role in the formation and maintaining the higher order structures of protein molecules.[3] Polyamides constitute an important group of synthetic polymers (e.g., nylons), wherein the role of H-bonding in determining crystalline structure has been proved critical.[9,10]

The role of H-bonding in polymer blends prompted intensive research toward a prediction of the phase behavior of polyamide blends with H-bond active polymers, e.g., PEO.[11,12] *N*-methylacetamide (NMA) has been long recognized as the smallest model compound most representative of the peptide (amide) group,[8] which continues to be extensively studied.[13–15] In spite of extensive studies of the apparently simple molecule of NMA, "the 1700 cm^{-1} to 1200 cm^{-1} region of NMA is probably the most discussed and controversial region of any molecule exhibiting a trans-secondary amide group."[16] Model studies of diamides[3] and other oligomeric amides and their H-bonded molecular assemblies[17–19] can be viewed as an introduction to the more complicated polyamide systems, in which simultaneous multiple interactions and crystallizability additionally complicate the interpretation of the data.[20,21] To distinguish between H-bonding phenomena in amorphous and crystalline solids, a series of *N*-alkyl and C-alkyl substituted amides was studied quenched in amorphous hydrocarbon matrices and, subsequently, crystallized upon heating.[3] A factor complicating H-bonding studies is water, traces of which are difficult to eliminate from hydrophilic systems like polyamides.[5] Various possible forms of H-bonding interaction between the amide groups, including one-dimensional chains and ladders, two-

dimensional sheets, and three-dimensional networks have been examined by *ab initio* calculations.[17,22]

HYDROGEN BONDING IN UREAS AND URETHANES

Similarly, H-bonding in polyurethanes,[23–25] polyureas,[7,26] and polyurethaneureas[27–30] has received considerable attention, although not on par with the scope of research in polyamides and peptides. Since the pioneering work of Born and Hespe,[31] in which the bifurcated character of the H-bonded structures in polyureas was established, papers have appeared dealing with the nature of H-bonding of urethane and urea segments in polyurethane/urea block copolymers by following the effects of temperature on the IR absorption spectra.[7,32] Simple, low molecular weight models of urethane, and urea compounds have been extensively studied.[7,27,33–36] They provided spectral characteristics critical in the studies of cooperative effects of various H-bonding groups, primarily bis-ureas, which are important in the interpretation of H-bonding segmented copolymers.[33,37] Bis-ureas have also recently been broadly utilized in tailoring materials via supramolecular chemistry[34–36] and in crystal engineering.[38] These experimental studies were complemented by the theoretical studies of various H-bonding oligourea aggregates, e.g., chains and ribbons.[39,40]

EXPERIMENTAL

Materials

In this study, telechelic siloxanes having number average molecular weight of $\sim$ 5000 g/mol were used. The synthesis of some of the materials used in this study: model amides: acrylamidoamido siloxane (ACMAS), methacrylamidoamido siloxane (MACMAS), and acrylamido siloxane (ACMS); and model ureas: methacryloxyurea siloxane (MAUS) and α-methylstyrylurea siloxane (MeStUS), were described in our previous paper.[1]

An additional model amide, methacrylamido siloxane (MACMS), was synthesized by reacting aminopropyl-terminated PDMS (molecular weight 5000 g/mol) with methacrylic anhydride at room temperature in heptane in the presence of a slight molar excess (10%) of triethylamine, followed by filtration and solvent evaporation. No attempts were made to purify the material of traces of the impurities (visible on the IR spectra). Chemical structures of the model compounds are included in the Appendix.

IR spectroscopy

Infrared spectra were recorded on a Thermo-Nicolet Magna 750 FTIR spectrometer using a heated cell with KBr windows (0019-200) manufactured by Spectra Tech with a controller manufactured by Omega (CN3000). The spectrometer was set to 4 μm resolution. The controller was programmed to ramp the temperature from 30°C to 150°C in 10°C increments (2 min ramps) with a 3-min hold at each temperature.

The thickness of the samples was maintained approximately constant by using 10 μm Teflon™ spacer between the KBr plates, but noticeable differences in the samples thickness were observed (by reference to the absorption of the vinyl groups). The polymer film samples were made by curing the reactive siloxanes, containing 0.2 wt % photoinitiator—Duracure™ 1173. Ultraviolet light (Sylvania™ Blacklight) was used to cure the samples directly between the two KBr plates using the 10 μm spacer to control the thickness.

RESULTS AND DISCUSSION

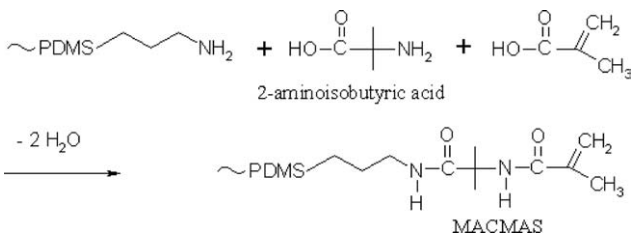
In almost all of the cases, the original spectra and the spectra at the end of the heating and cooling cycle were nearly identical, with the only detectable difference being the level of absorbancy due to changes of the sample thickness. Considering the potential heat instability of the urea groups, additional samples of MAUS (fluid and film) were heated up to 170°C, but even in this case, the spectrum returned to its original pattern after the heat cycle. In our discussion, we put much more emphasis on observed trends than on the specifics of the spectra. Specifically, no peak assignments were attempted beyond what was referenced in the literature, as we are convinced that a thorough analysis of the spectra would require much more in-depth studies.

As we have stated earlier, by studying our chosen end-groups essentially immersed in a silicone medium, we can model them as an unperturbed state of small clusters in dynamic equilibrium. By UV-activating covalent crosslinks within the endgroups, we can then transform our liquid samples to solid films and so study their H-bonding abilities in a conformationally restricted environment. Our analysis will examine first the amide endgroups and then the urea endgroups.

Model amides

A comparison of four model amides was performed: (a) ACMS: having acrylamide groups directly connected to the alkyl group of telechelic PDMS, (b)

MACMS: with methacrylamide groups directly connected to the alkyl groups of PDMS, (c) ACMAS: having acrylamide groups linked to another amide group which functions as a spacer connecting the acrylamide groups to the alkyl group of PDMS, and (d) MACMAS: having methacrylamide groups linked to the amide spacer. Thus, ACMS and MACMS are N-substituted monoamides (however, large the substituent is), whereas ACMAS and MACMAS can be considered as models of dipeptides, as the two amide groups are separated, as in polypeptides, with a single CR_n group. Both ACMAS and MACMAS can be considered as products of the amidization of 2-aminoisobutyric acid



with the end-functional 3-aminopropyl PDMS, and acrylic or methacrylic acid, respectively. Whereas the standard model compound for studies of the peptide group is NMA, not withstanding all of the difficulties associated with its analysis,[16] we are not aware of any convenient models for experimental studies of oligomeric peptides in spite of all the interest in such materials.[17]

In our model polymers, endgroups are free to interact within the discrete phase-separated domains which form the junction points of the transient silicone networks. In fact, these domains are formed primarily because of the interactions between the endgroups and their incompatibility with the polysiloxane carrier-molecules to which they are attached. Within these domains, we expect that, subject to steric constraints, H-bonding segments become arranged adjacent to each other, thereby lowering the energy of the domain. Some of such possible arrangements are shown in Figure 1 in a two-dimensional representation, limited to four molecules for simplicity. These schematics are applicable to all groups (such as amides and ureas) able to form strong, directional hydrogen bonds, hence the two-dimensional asymmetric schematic shape of the groups indicating hydrogen-bonding donor and acceptors "sides" or sites. Because these molecules are in dynamic equilibrium, their relative orientations can change and assume any of a number of other orientations (including out-of-plane orientations that would be difficult to show in our two-dimensional schematics). If we accept this reasoning, then it is clear that an infrared spectroscopic analysis would average over both a macroscopic volume of

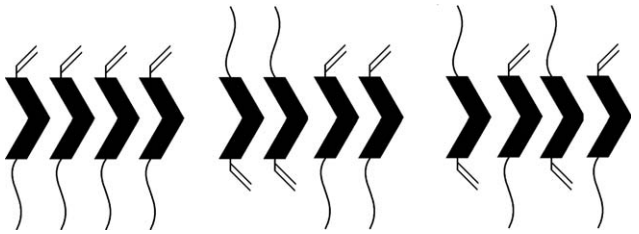


Figure 1 Schematic two-dimensional representations of some possible domains consisting of four endgroups.

sample containing a huge number of such domains and a length of time very long compared with the time of dynamic rearrangements it might take a domain to switch configurations. Because each of these different orientations has a slightly different infrared energy absorbance in the regions we display, the affect of such averaging would be to produce fairly complex signals that are rich in data but difficult to analyze unambiguously. This is indeed what we observe.

This complexity would exist even if all the domains consisted of only four different molecules. But if we accept that the number of endgroups within a domain may vary both across our macroscopic sample and also may vary in time for any given domain, then our signal complexity becomes even greater.

If the vinyl end-groups of the telechelic siloxanes are free-radically crosslinked (oligomerized) leaving no unreacted species (high degree of conversion observed, as discussed previously[1]), one might expect this domain to transform into either a tetramer or two dimers.

In keeping with the schematic representations, one can imagine a four end-group crosslinking site to form H-bonding aggregates either involving all four groups, or the two pairs of dimers, as schematically shown on Figure 2 and Figure 4, respectively.

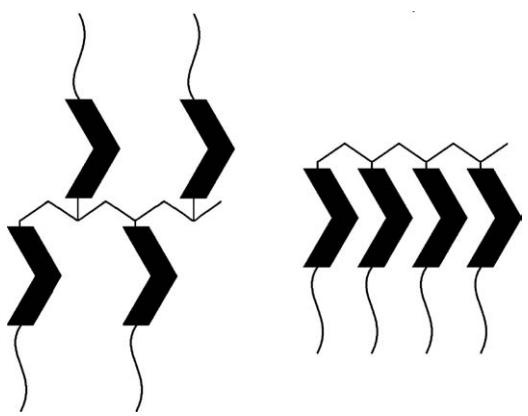


Figure 2 Schematic two-dimensional representation of some possible configurations of four endgroups crosslinked into a tetramer within a domain.

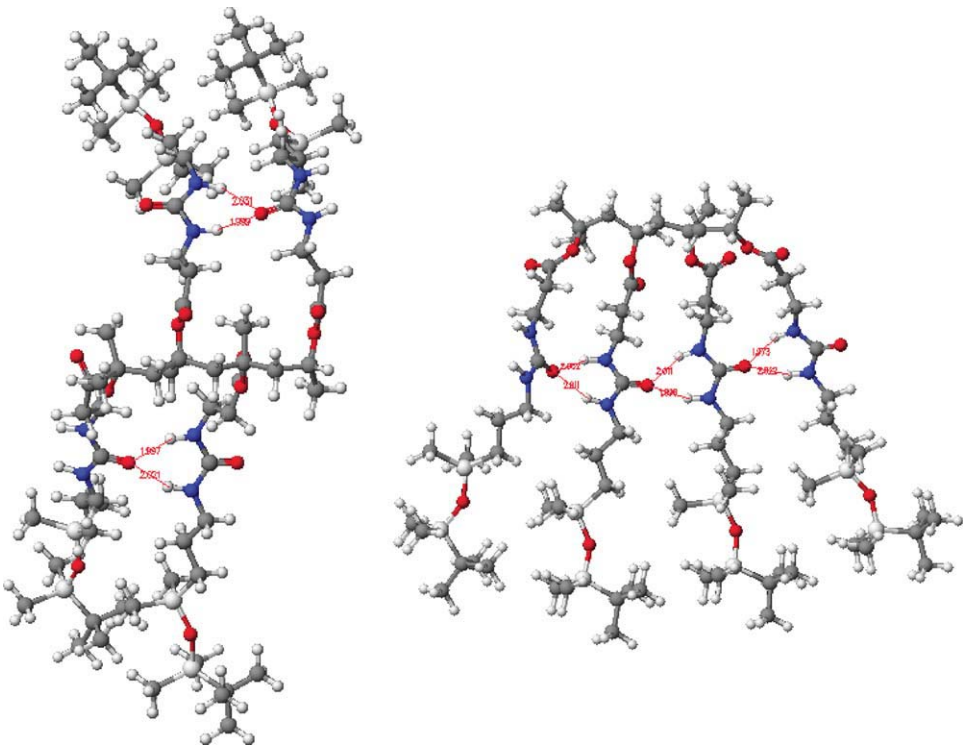


Figure 3 Molecular models of the two configurations shown in Figure 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This is perhaps easier to envision on the molecular model of tetramers shown in Figure 3, where the oligomerized end-groups of the MAUS are shown, with the H-bonds marked. (For simplicity, the long siloxane chains are represented by one, bulky siloxy unit attached to the urea links).

If two dimers (rather than a tetramer) are formed by the oligomerization within a domain containing four reactive end-groups, they can also form different H-bonded aggregates, for instance those represented schematically in Figure 4.

Note that for such crosslinked aggregates, having no unreacted groups, there would always be one unmatched H-bond donor site and one unmatched H-bond acceptor site for the tetramer aggregates and for configurations similar to the first schematic in Figure 4. Correspondingly, there would occur two of each of acceptor and donor sites for configurations similar to the second schematic in Figure 4, with characteristic high wavenumber absorption signals in both C=O stretching and the N—H stretching regions. The current literature refers to such signals as originating from the "end-group-free" species.[5]

When enlarging our view to domains containing other than four endgroups, we can easily imagine that complexity within the solid film spectra would again be the rule. Even though we expect the domain arrangements to be independent of time for a crosslinked film, except for a short range dynamic fluctuations, they should still include a large number of different arrangements within a macroscopic sample volume. In a manner similar to that mentioned earlier for liquid state, the absorbance signal will be an average of different numbers of unmatched (free) donor and acceptor sites. However, one would expect the spectra to show a temperature dependence as the H-bonding interactions between various oligomers within the crosslinking sites (domains) could vary.

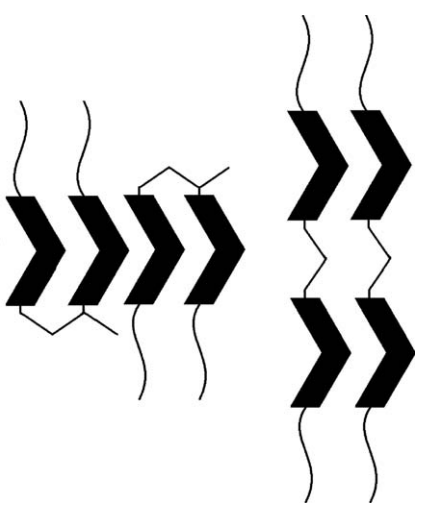


Figure 4 Schematic two dimensional representations of some possible configurations of four endgroups crosslinked into two pairs of dimers.

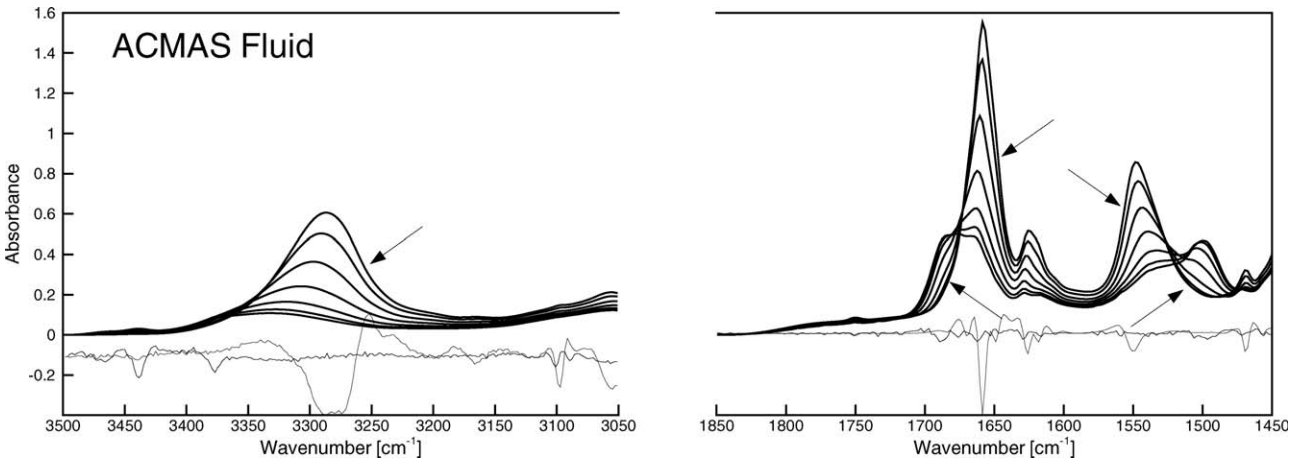


Figure 5 IR absorbance of ACMAS fluid.

In comparing various telechelic amide siloxanes, the most noticeable and surprising feature (which in fact inspired the study of the model siloxanes described here) was a strong difference observed between ACMAS and MACMAS. The only difference in the molecular structures of these two siloxanes, both having two amide groups at each end of the polymer chain, is that the latter has a methyl-substituted terminal acrylamide group. Yet, as reported earlier,[1] the viscosities of the corresponding fluids differ very significantly: 49,000 cps for ACMAS versus 3300 cps for MACMAS at 25°C for the 5000 g/mol fluids. This viscosity difference suggested that the H-bonding of terminal groups of these two model polymers is very significant considering that both end-groups can be viewed as model dipeptides, N-substituted with huge, yet very accommodating substituent silicone chains. Here, we show that the IR spectra of ACMAS and MACMAS also demonstrate some relevant differences.

In the discussion that follows, we will attempt to highlight the influence an additional terminal methyl group has on the behavior of both the ACMAS endgroups, and on the simpler, monoamide ACMS. In a similar way, we will also highlight the influence of the insertion of a second backbone amide molecule as a spacer on the ACMS and the MACMS endgroups. Lastly, we will discuss features that can be noted upon covalently crosslinking these four types of endgroup aggregates.

The influence of a terminal methyl group

Figures 5 and 6 show the IR spectra of ACMAS and MACMAS, and Figures 7 and 8 show the IR spectra of ACMS and MACMS, all for the liquid (uncured) samples. Each spectrum shows Absorbance in the N—H stretching region ($\sim$ 3200–3400 cm^{-1} wavenumbers), Amide I region ($\sim$ 1630–1700 cm^{-1} wavenumbers), and Amide II regions ($\sim$ 1490–1570 cm^{-1} wavenumbers). Also included are the "end-group-free" and "truly free" regions around 3400–3500 cm^{-1} wavenumbers. Curves are shown for temperature scans at 30°C, 50°C, 70°C, 90°C, 110°C, 130°C,

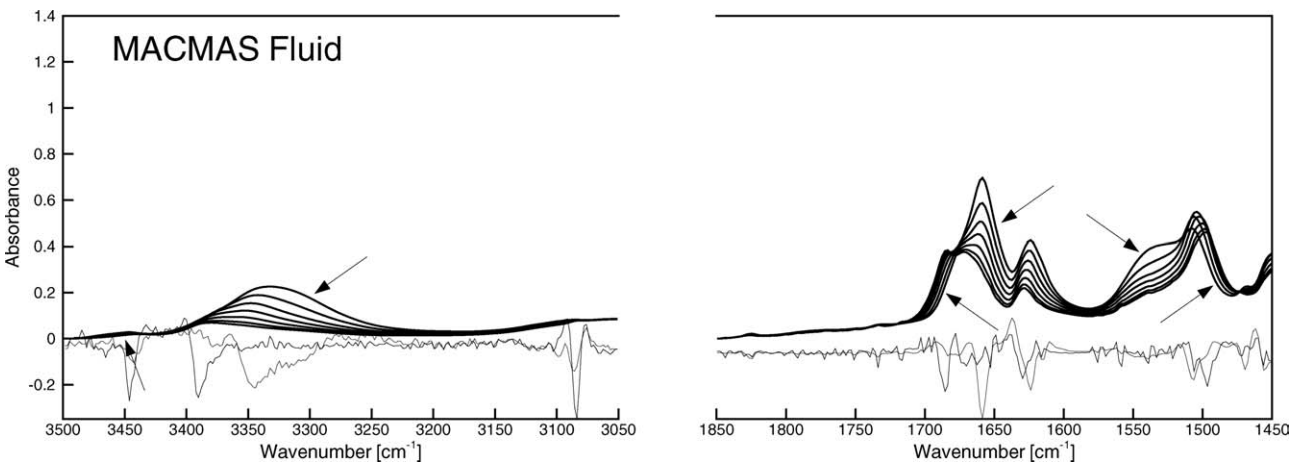


Figure 6 IR absorbance of MACMAS fluid.

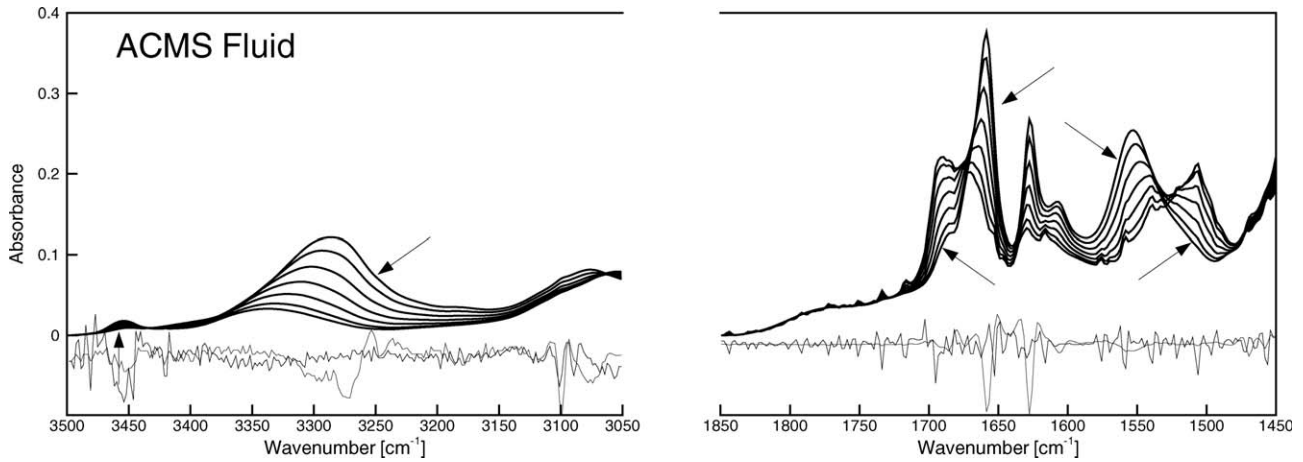


Figure 7 IR absorbance of ACMS fluid.

and 150°C. Second derivative curves (in arbitrary units and offsets) are shown below the absorbance plots, with the gray curves corresponding to the 30°C data and the black curves the 150°C data. The arrows indicate the direction in which the regions of the spectra change with increasing temperature.

A comparison of the spectra of ACMAS and MACMAS points out some very significant differences, especially in the Amide II region. The Amide II range of MACMAS at room temperature already looks similar to the high temperature spectrum of ACMAS in this range, pointing out substantial changes in the H-bonded aggregates between the two. However, these differences are mainly observed in a range (Amide II) which corresponds to a complex mixture of absorptions modes, primarily C—N stretching and N—H bending, and are so rendered difficult to interpret. The effect of the methyl group on the Amide II band is also visible in comparing ACMS and MACMS, the latter having its absorption signal shifted toward the lower frequency range (weaker H-bonding), but the spectra do not differ qualitatively.

However, in the Amide I range, MACMAS absorbs at room temperature in a manner very similar to ACMAS, they both have major signals near 1655–1660 cm^{-1}, but with a lower intensity. MACMAS also shows at room temperature a more pronounced high wavenumber shoulder and its absorption band undergoes a greater relative change in magnitude with temperature than ACMAS, pointing to weaker H-bonding in MACMAS.

The N—H stretching bands also seem to provide some clues regarding the structure of the H-bonded clusters. We observe multiplets on the second derivative spectra in the H-bonded ranges, at much higher wavenumbers for MACMAS than for ACMAS, which are significantly affected by temperature changes. We also observe different types of signals in the "free" N—H stretching region around 3450 cm^{-1}, which might be attributed to "truly free" and "end-group-free"[5] N—H vibrations. The fact that the position of

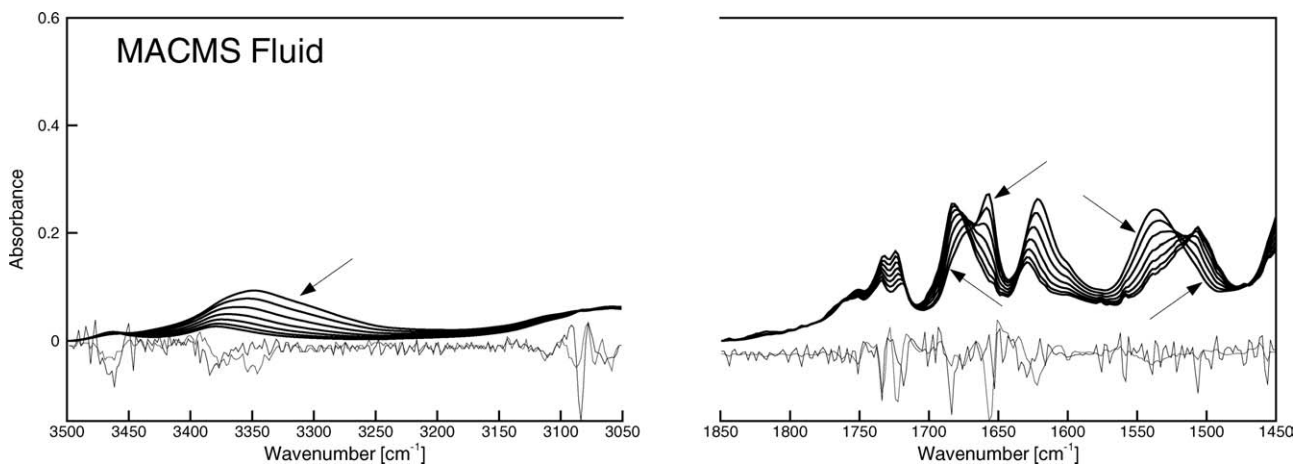


Figure 8 IR absorbance of MACMS fluid.

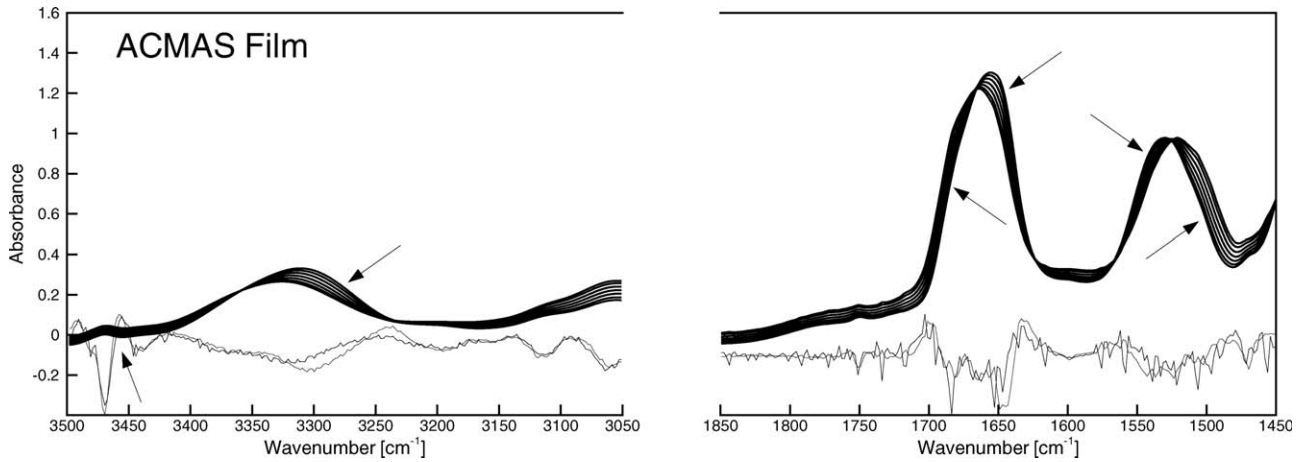


Figure 9 IR absorbance of ACMAS film.

the N—H stretching band attributed to N—H bonding species falls into a lower wavenumber field for the acrylamide than for the methacrylamide derivatives, perhaps also pointing out a perturbation of the H-bonding in the methacrylamide group due to the proximity of the methyl group.

The very strong effect of the methyl group on the spectra observed in diamides is less pronounced in the comparison of the monoamides, ACMS, and MACMS. We included these two species into this study seeking a simpler model to confirm the effect of the methyl group on the spectra. Also in this case, a much stronger temperature dependence of the IR spectra was observed in MACMS than in ACMS, particularly in the Amide I range.

Significantly for MACMS, no unexpected shift of the room temperature position of the Amide II band was observed relative to ACMS, showing that the presence of the methyl group has the most important effect on some modes of vibrations/H-bonding within the clusters of diamides. On the other hand, the presence of the methyl group, both in amides (MACMS) and diamides (MACMAS), significantly (by $\sim$ 50 cm^{-1}) affects the room temperature position and the shape of the N—H stretching band for the H-bonded groups, when compared with their peers (ACMS and ACMAS, respectively).

The effect of the insertion of a second amide group as a spacer

In comparing monoamides with diamides, it is evident that the diamides have stronger [for instance, in the case of ACMS (one amide group) vs. ACMAS (two amide groups) much more than double] absorption signals in both the Amide I and N—H stretching regions when using the vinyl group absorption as a standard. This behavior clearly points to much stronger H-bonding of the diamides perhaps because of their ability to form multiple H-bonds. The formation of relatively strong signals at higher temperatures corresponding to "free" N—H stretching in ACMS also points to a relative weakness of the H-bonding of ACMS when compared with ACMAS. Although the position of the Amide I

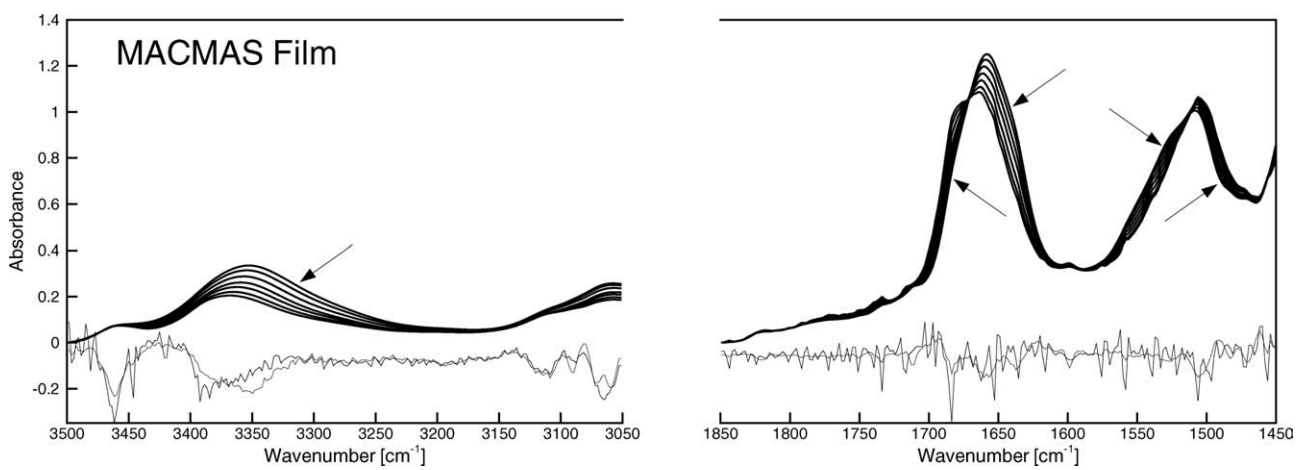


Figure 10 IR absorbance of MACMAS film.

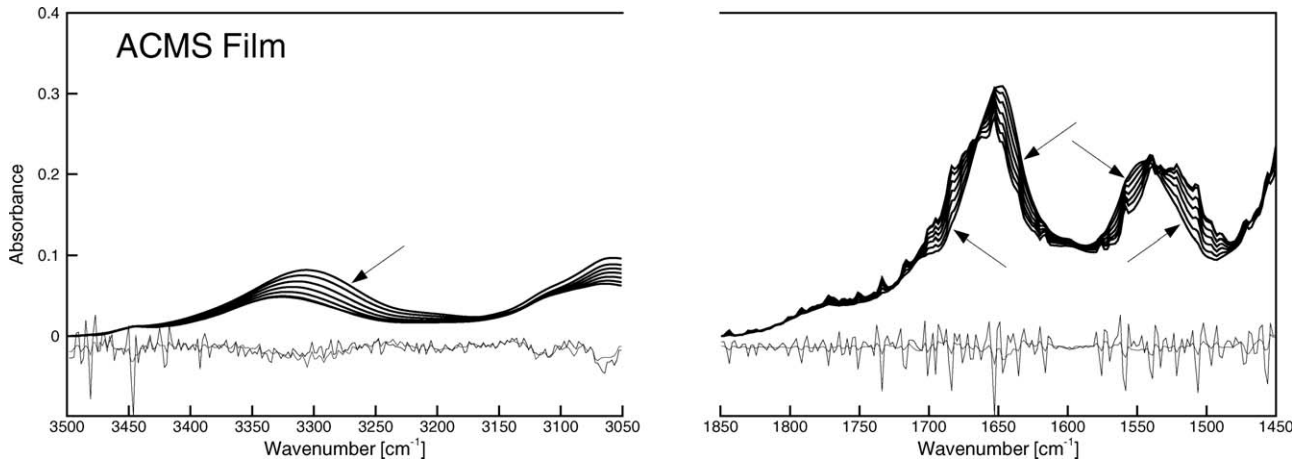


Figure 11 IR absorbance of ACMS film.

signals at room temperature is not strongly affected in any of the amides studied, the influence of an additional amide group as a spacer is visible in comparing the Amide II and N—H stretching bands of MACMS with MACMAS. The unique characteristics of the room temperature spectrum of MACMAS in the Amide II range, as previously discussed, are entirely correlated to the presence of the additional amide group linking the methacrylamide group with the silicone chain. The effect of the amide spacer group is also reflected in the N—H stretching band. The lower wavenumber range N—H absorption of MACMAS suggests the formation of stronger H-bonding aggregates than observed in MACMS. This effect of the additional amide group is not that well pronounced in the comparison of ACMS and ACMAS in the N—H stretching region.

The influence of covalent bonding (curing of the liquid amide rubbers into solid films)

Clearly, much can be observed when amides or diamide end-groups can freely assemble in fluids with no restrictions regarding their mutual positions. An analysis of the spectra of the corresponding films in which H-bonding groups are attached as substituents to the oligo(meth)acrylamide chains should provide additional information regarding the interactions between those groups under spatial restrictions. Spectra of the films plotted in the same manner as that used earlier for the fluids are shown in Figures 9 and 10 (ACMAS and MACMAS films, respectively), and Figures 11 and 12 (ACMS and MACMS films, respectively).

The IR spectrum of ACMAS and, to some extend, also of MACMAS film in the entire range are rather weakly affected by temperature. However, their absorptions bands seem to be considerably more complex (broader signals) than those observed in the spectra of the corresponding fluids, which might indicate that a variety of H-bonding aggregates is formed upon the curing (oligomerization) of (meth)-acrylamide groups. Significantly, the easily detectable signals of "free" N—H groups (very weak in the ACMAS fluid) might point to the unavoidable presence of "end-group-free" groups within the cross-linked domains (discussion of Figs. 2 and 4).

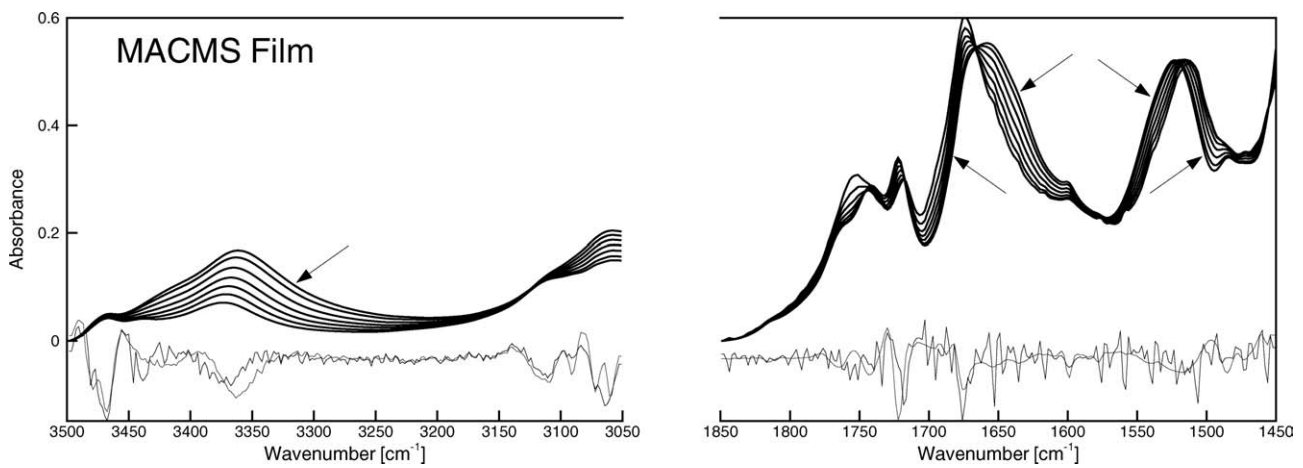


Figure 12 IR absorbance of MACMS film.

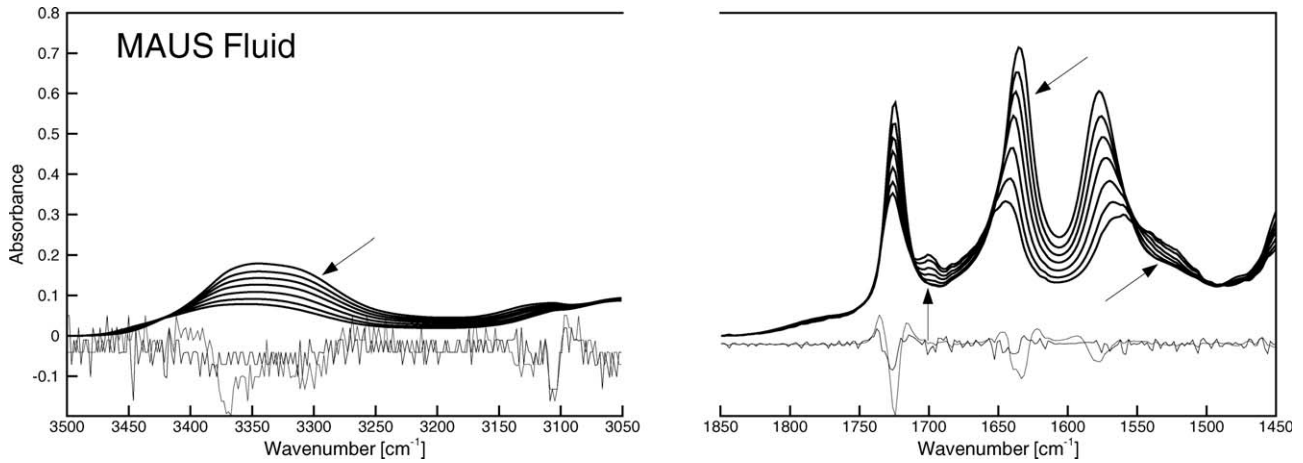


Figure 13 IR absorbance of MAUS fluid.

The fact that MACMAS film has an Amide II band near 1500 cm^{-1}, much lower than ACMAS film, and that MACMS film also has a lower wavenumber signal in this region than ACMS film indicates that the methyl groups in these materials (now part of the oligo(meth)acrylamide chain) can still affect the H-bonding abilities of the pendant diamide (MACMAS) or amide (MACMS). We note that these are no different otherwise from the pendant groups of ACMAS and ACMS, respectively, and find that observation rather surprising! This could perhaps reflect a change of mechanism from a structural (steric) hindrance of H-bonding by the methyl substituent of methacrylamide group to a conformational/rotational hindrance to alignment due to the constraints created by the oligo (methacrylamide) chains.

The presence of "free" N—H stretching signals in the spectra of the films is perhaps less surprising, considering that not all the groups within the aggregate (originally freely interacting with each other in the liquid state) would became part of the same oligomers. However, even if they would be part of the same oligomers, there would still be "end-group-free" N—H groups (and, correspondingly, unmatched C=O groups). Statistically, the smaller the oligomer formed the larger the concentration of the "end-group-free" groups. Dynamic equilibrium between H-bonding groups within the same crosslinking site (aggregate) is possible (compare the schematic configurations of Figs. 2 and 4), which might be responsible for the surprisingly strong temperature dependence of the spectra of some of the films (especially visible on the spectra of MACMS, but also on MACMAS).

Model ureas

The importance of models for IR studies of urea groups stems from a strong interest in polyurea/urethane polymers wherein H-bonding is the primary force controlling the mechanical properties. It also derives from the recent trend in using strongly interacting bis-urea groups in supramolecular chemistry and crystal engineering. It appears that there are fewer papers dedicated to this field than there are to the amides, and that this might be partially due to the lack of good model compounds to study. In this

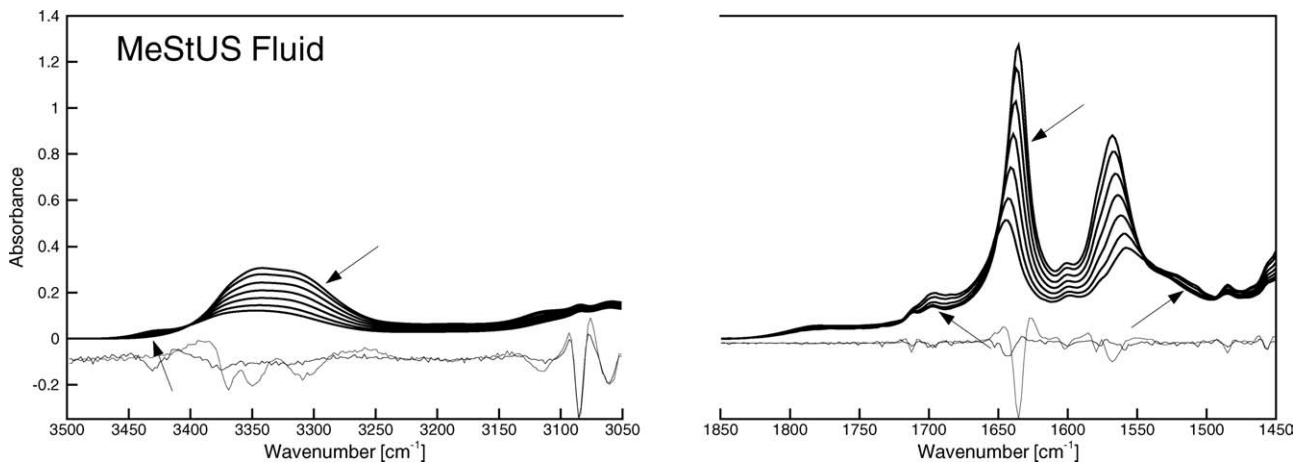


Figure 14 IR absorbance of MeStUS fluid.

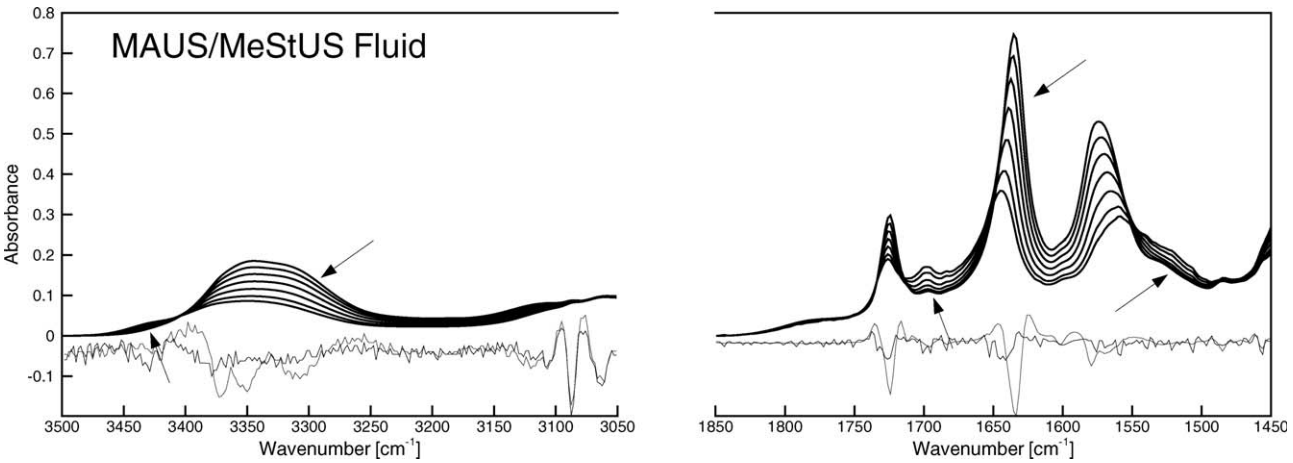


Figure 15 IR absorbance of MAUS/MeStUS fluid.

article, we present two model ureas: MAUS and MeStUS, both carrying free-radically (co)polymerizable end-groups. MAUS is capable of both homo- and co-polymerization, whereas MeStUS (having α–methylstyryl reactive end-groups) can only be copolymerized with other free-radically polymerizable groups, such as, the meth(acryloxy) groups of MAUS. Consequently, in addition to the analysis of the two liquid silicone ureas, an equimolar blend of MAUS and MeStUS was also studied, and such a blend was subsequently polymerized to form a film.

Urea fluids

Figures 13–15 show the IR spectra of MAUS and MeStUS fluids and of their equimolar blend. Each spectrum shows absorbance of the N—H stretching region, and C=O stretching and CNH bending regions in the same manner as shown earlier for the model amide fluids and films.

As expected, the IR spectra confirm the formation of strong H-bonds in both ureas studied. "Amide I" signals (C=O stretching) of both MAUS and MeStUS appear in the low wavenumber field (near 1630 cm^{-1}), characteristic of "ordered" clusters, and their peak locations are relatively weakly affected by temperature. The appearance of the higher wavenumber H-bonded C=O signals responsible for the broadening of the band at higher temperatures is, however, accompanied by the appearance of signals characteristic of "free" C=O groups near 1700 cm^{-1}.

The "Amide II" region is also relatively weakly affected by changes in temperature, although an expected shift of the band toward lower wavenumber absorption with increasing temperature is observed.

The N—H stretching band is surprisingly complex showing bi- or even multi-modal bands (broader in the case of MAUS) of H-bonded vibrations, which are relatively weakly affected by temperature. A weak high wavenumber shoulder, attributable to absorption in the "free" N—H stretching region becomes somewhat more pronounced as temperature increases. The fact that this weak signal appears near 3430 cm^{-1} (at a much lower wavenumber than observed in amides) might suggest that it mostly corresponds to "end-group-free" vibration of the N—H group.

The influence of covalent bonding (curing the liquid urea rubbers into solid films)

The spectra resulting from covalently crosslinking the MAUS and MAUS/MeStUS fluids into solid films are shown in Figures 16 and 17.

The N—H stretching band signals do not differ from their corresponding fluids with the exception that the high-wavenumber shoulders are more prominent even at low temperatures. Close similarity of the spectra of MAUS and MeStUS fluids and of the corresponding films suggests that interactions within the clusters are similar and are not affected by any conformational restraints due to chemical connection of the end-group to the vinyl chain. The fact that the signals attributable to "free" groups are more visible in the spectra of the film might suggest the formation of a relatively greater number of smaller aggregates within a crosslinking domain upon polymerization ("end-group-free" signals), which could also explain the rather significant temperature dependence of those signals.

An additional measure of the strength of the interactions between the urea groups is the fact that the proximity of the two very different groups (the comparatively small alkyl-methacrylate for MAUS and the bulky substituted alkyl-aryl for MeStUS) has a relatively weak effect on the spectra characteristics of either the fluids or the films. In fact, the temperature dependence of the spectra of MeStUS fluid appear to be weaker that of MAUS, in agreement with the rheology data.[1] This may suggest that the phenyl ring plays some role in aligning and stabilization of the H-bonded structures.

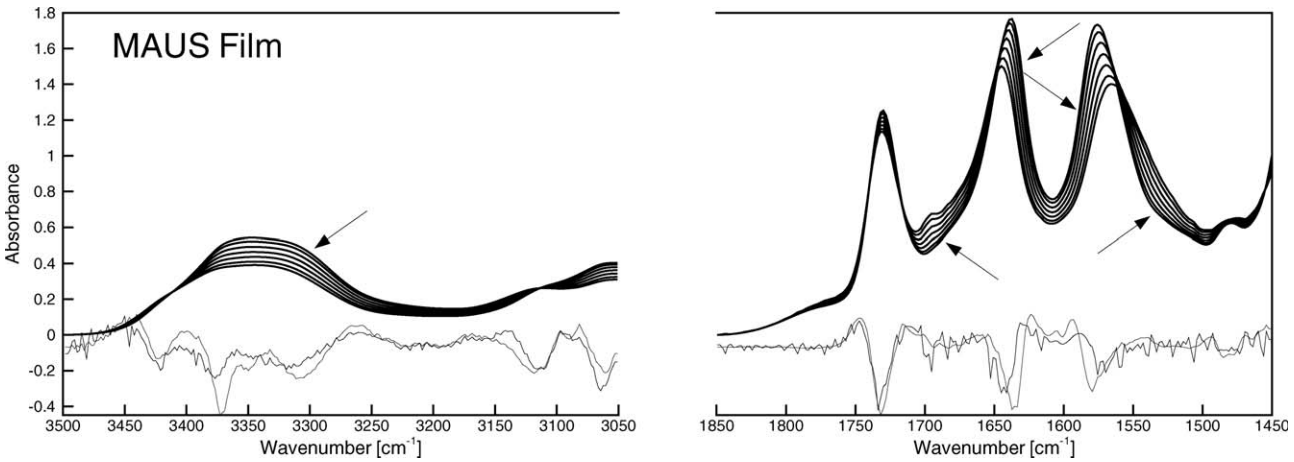


Figure 16 IR absorbance of MAUS film.

Finally, we observe that the temperature dependence of the two ureas film spectra in their entire range seems to be surprisingly weak even in comparison with the strongest H-bonding diamide (ACMAS).

CONCLUSIONS

In presenting data regarding H-bonding phenomena of model amide and urea groups studied in an idealized environment, we wanted to provide examples of convenient models for in-depth studies of two broad classes of H-bonding groups. The telechelic siloxanes drive the polar end-groups into phase-separated domains in which the groups can freely assemble to form H-bonded clusters. In spite of the fact that small clusters of the end-groups could be expected to exist in the discrete domains, fairly complex vibrational spectra result from the change of relative orientations of the groups in a state of dynamic equilibrium.

By the polymerization (oligomerization) of the vinyl end-groups of those telechelic polymers, a complementary set of model networks is formed. This allowed us to study the H-bonding interactions between the amide and urea groups in the more constrained environment of the crosslinked domains of those networks.

In the liquid amide series, the difference between ACMAS and MACMAS (models of diamides) is most remarkable wherein the presence of the methyl group in one of the amide groups (methacrylamide group of MACMAS) not only causes very significant differences in the Amide II region of the spectra but also makes the H-bonding in MACMAS much more temperature dependent. These differences in H-bonding strength between ACMAS and MACMAS are responsible for the observed differences in viscosities between these two model polymers.[1] This strong effect of the methyl group is, however, mostly observed in the case of diamide (MACMAS) and is not well pronounced in comparing the monoamides (ACMS and MACMS).

Remarkably, the presence of the methyl group in MACMAS has a significant effect also on the spectrum of the film when compared with ACMAS. It is

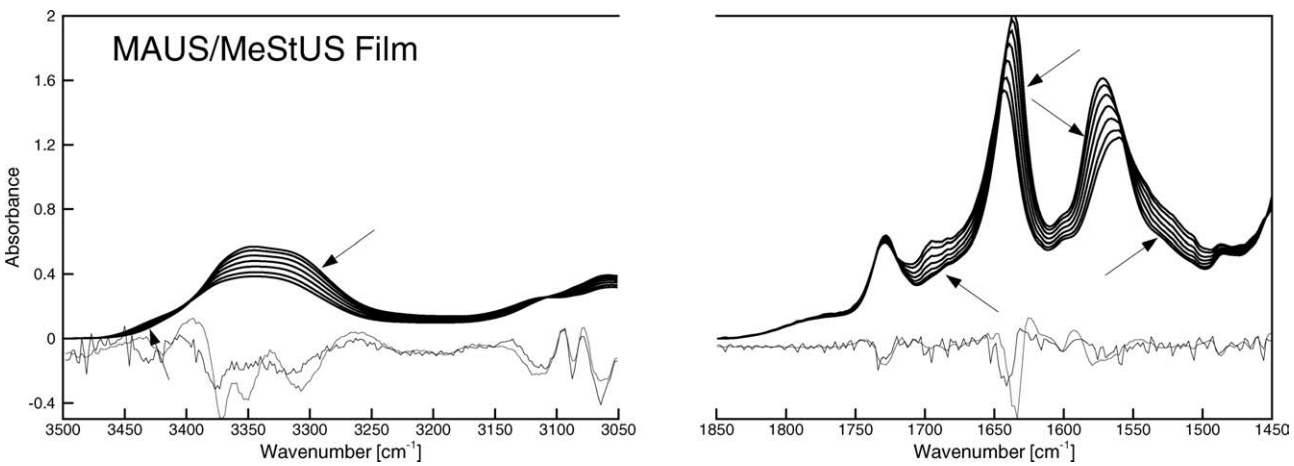


Figure 17 IR absorbance of MAUS/MeStUS film.

not clear how the presence of the methyl group could affect the IR spectra of the neighboring amide groups when it is a part of the oligomeric chain, although some hypothetical interpretation has been suggested. Considering a complete conversion of the reactive vinyl end-group, the signals attributable to "free" H-bonding groups in the films can most likely be representative of "end-group-free" groups.

The hydrogen bonding in the liquid model ureas, both MAUS and MeStUS, appears to be strong, as judged by the position of the C=O stretching bond in a range attributable to highly ordered H-bonding clusters.[29] It is also less affected by temperature, which is in agreement with the temperature dependence of the viscosity of those materials, as reported earlier.[1] A closer examination of the absorption spectra in "free" regions indicate that in the films there are lower frequency signals in both C=O and N—H stretching regions, as expected for the "end-group-free" species which should be dominant in the completely oligomerized crosslinking sites of the films.

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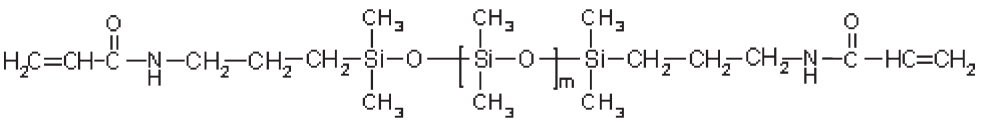
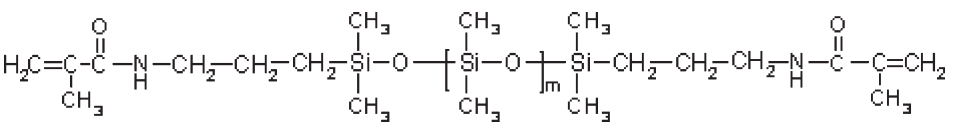
APPENDIX

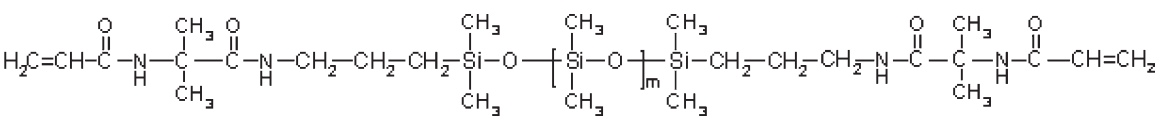
ACMS (Acrylamido siloxane)



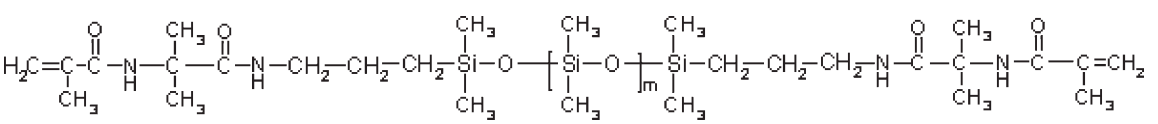
MACMS (Methacrylamido siloxane)



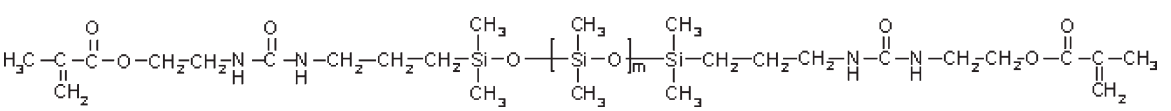
ACMAS (Acrylamidoamido siloxane)



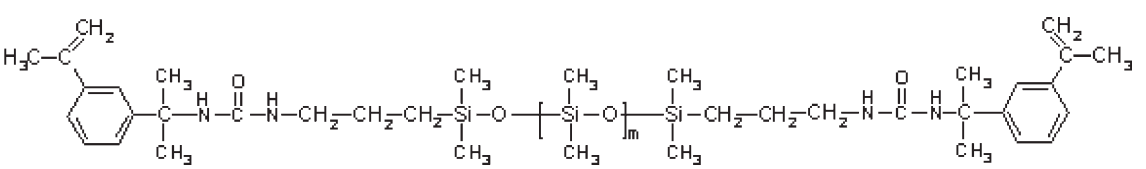
MACMAS (Methacrylamidoamido siloxane)



MAUS (Methacryloxyurea siloxane)



MeStUS (α-Methylstyrylurea siloxane)



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