

Polyurethanes via Microemulsion Polymerization

John Texter* and Paul Ziemer

College of Technology, Eastern Michigan University,
Ypsilanti, Michigan 48197

Received March 26, 2004

Revised Manuscript Received June 11, 2004

Microemulsions are three or more component solutions comprising two immiscible liquids, typically water and oil. Miscibility is induced by a third amphiphilic component or surfactant. Since their discovery by Hoar and Schulman over 60 years ago,¹ much theoretical and experimental development has transformed microemulsion science and technology into a mature field.^{2–4} Microemulsions are usually expressed as oil in water solutions wherein nanoscopic oil droplets (2–6 nm in diameter) are dispersed in water with the aid of a low radius of curvature surfactant. Reverse or inverse microemulsions have nanoscopic water droplets dispersed in a pseudo-continuous phase of oil, and the low radius of curvature in this case has opposite sign to the radius of curvature in the oil in water example. Since the droplets or domain lengths in such systems are nanoscopic, light is only very weakly scattered by the droplets, and such microemulsions appear to be transparent. A particularly interesting property of microemulsions is that when the oil and water and surfactant are suitably balanced, droplet “microstructure” can be replaced in part by a random bicontinuous structure comprising interdigitated water and oil domains, so that such a solution is effectively continuous in both water and oil.^{5–7} The average curvature in such systems is typically close to zero and comprises essentially equal amounts of positive and negative components. Such bicontinuous structures are of keen interest because they afford pathways of diffusive transport. Furthermore, on occasion the water component is replaced with some other immiscible liquid, typically a polar solvent of some kind, and in this report we utilize propylene glycol as such a “water replacement”.

Microemulsion polymerization has heretofore been confined to examples wherein the oil or water domains, or both domains, comprise radical chain polymerization of monomers such as acrylates. A rich literature^{8–13} has been developed around such radical chain polymerization in microemulsions, and microlatexes of various monomers have been produced by incorporating oil monomers in oil in water microemulsions or by incorporating hydrogel monomers in water in oil microemulsions. In addition, nanoporous membranes have been produced by polymerizing bicontinuous microemulsions of radical chain polymerizing monomers.^{14,15}

This communication reports the first application of microemulsion polymerization to produce polyurethanes. Polyurethanes form by addition step polymerization of diols with diisocyanates (radical chain polymerization is not involved). When the mole ratio of monomers is 1.00 ± 0.01 , urethane polymers having more than 100 repeating pairs of monomers may be

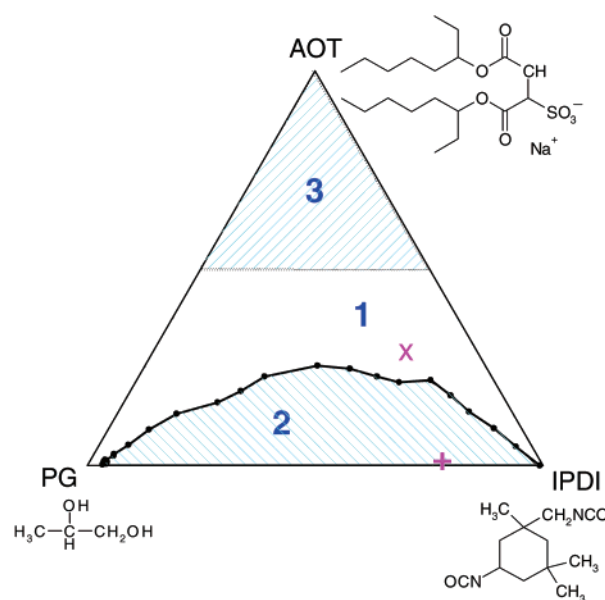


Figure 1. Room temperature ternary phase diagram illustrating large single-phase microemulsion region 1. The region 3 above 50% (w/w) AOT was not explored; the multiphase domain 2 comprises PG in IPDI and IPDI in PG microemulsions emulsified in each other. The “X” and the “+” represent loci of polymerization.

obtained.¹⁶ High molecular weights are usually obtained by incorporating cross-linking agents.

We apply microemulsion polymerization here to immiscible monomers: propylene glycol (PG) and isophorone diisocyanate (IPDI). We use bis(2-ethylhexyl) sulfosuccinate, sodium salt (AOT), as the surfactant. AOT is widely appreciated as an excellent surfactant for producing reverse microemulsions of water in oils and monomers and for producing nonaqueous microemulsions with such polar liquids as PG, ethylene glycol, etc.^{17–19} The production of polyurethanes from immiscible monomers has limited applications, since stirring and emulsification are physically required until the reaction generates sufficient heat to carry itself forward. Nonstirred applications (such as injection molding) are unsuitable if the polymerization half-life is longer than the lifetime of the emulsion. Since microemulsions are thermodynamically stable solutions of the constituent components, mixing is driven by chemical free energy, and shear or stirring is not required to maintain a single-phase solution of the otherwise immiscible components.

A starting point for appreciating microemulsions is to construct a phase diagram to distinguish single-phase microemulsion domains from liquid crystalline domains and multiphase domains. In Figure 1, we present a ternary phase diagram for the PG/IPDI/AOT system at room temperature (22 ± 1 °C). Three domains are identified. Domain 3, above 50% (w/w) in AOT, was not investigated, as we have not explored the structure or properties of this domain. The cap of this domain, AOT, is a waxy, amorphous solid (this is the natural physical state; AOT cannot be crystallized since it contains three chiral centers). Another prominent domain is the emulsion domain 2, which is a multiphase domain that comprises two microemulsion phases: an IPDI in PG

* Corresponding author. E-mail jtexter@emich.edu.

microemulsion phase and a PG in IPDI microemulsion phase. Much more detailed composition, density, and tie-line analyses are required in order to confirm the phase structure of domain 2. Domain 1 is a single-phase microemulsion domain. It extends from the IPDI corner over to the PG corner, so that over some intermediate composition interval it necessarily contains irregular bicontinuous microstructure.

While each of PG and IPDI has a small but finite solubility in the other, as illustrated in Figure 1 along the PG–IPDI axis, the entire domain 1 is “heterophase” only in the “pseudophase approximation” where, for convenience, swollen microemulsion droplets (of PG in IPDI or of IPDI in PG) are considered to be a disperse pseudophase and the IPDI and PG, respectively, are considered continuous pseudophases. We wish to stress, however, that domain 1 is in fact simply a complex solution containing exotic complexes of surfactant (AOT), PG, and IPDI.

While there is ample evidence in the literature^{17–19} that PG and other polar organic solvents (e.g., ethylene glycol, dimethylformamide) form reverse micelles with AOT, and the ternary diagram exhibits a multiphase emulsion domain 2, it was suggested that a simple light scattering experiment might be beneficial to establishing domain 1 as a true microemulsion domain (rather than a molecularly disperse solution without surfactant aggregation). To this end, a series of AOT in IPDI solutions were prepared at concentrations of 0, 2.5, 5, 7.5, and 10% (w/w). These solutions were examined by dynamic light scattering in a Brookhaven Instruments 90Plus spectrometer, wherein scattered light intensity was examined at a scattering angle of 90°. Before measurement these samples were filtered through a 220 nm filter in order to exclude large particle or dust effects. The apparent mean log–normal diameters for concentrations of 5, 7.5, and 10% AOT increased in the order 5.9, 9.5, and 13.3 nm, respectively. The 0% control produced no measurable scattering, and the existence of scattering for the 2.5% sample was equivocal. The dramatic increase in the apparent size results from collective scattering, and examination of the correlation functions in each case showed a very significant collective scattering component with markedly slower decay than the initial, nanometer-scale, component. Plotting $1/d_{app}$ as a function of the % AOT and extrapolating to 0% AOT by linear regression yielded an estimate of 3.8 nm for the micellar size. Given that the length of an AOT ion pair is approximately 1.4 nm in longest dimension, this extrapolated estimate appears to be reasonable. The dramatic collective scattering components seen in each case and evidenced by the very strong apparent increase in micellar size with increasing concentration unequivocally supports the existence of reverse micelles in the AOT/IPDI system and the swelling of these micelles by addition of the IPDI-immiscible PG.

The structure of this microemulsion domain 1 will be investigated in further detail subsequently by conductivity and small-angle neutron scattering studies. For our purposes in this communication we want to focus on the “reverse” microemulsion domain closer to the “oil” or IPDI corner.

A molar equivalence between PG and IPDI is obtained at about 19.5% w/w PG, relative to PG and IPDI. Our initial polymerization attempts examined catalyst levels in microemulsions situated at 15% (w/w) PG with 85%

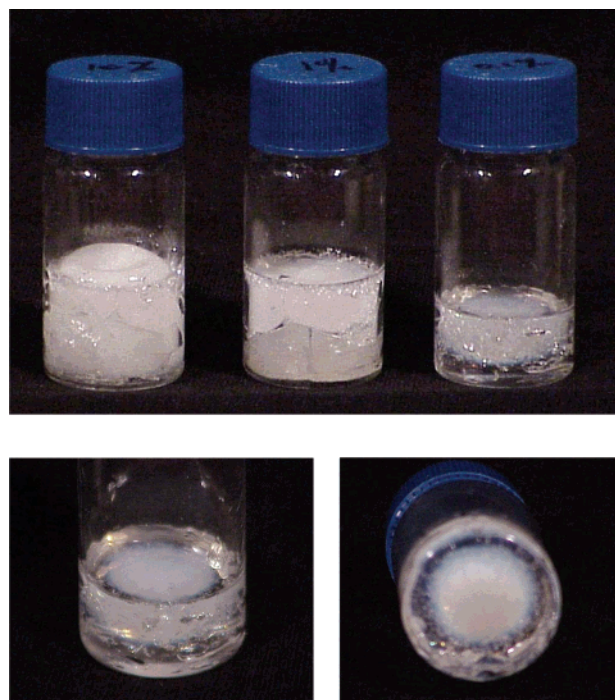


Figure 2. Illustration of initially observed frontal polymerizations described in the text. The upper sequence, left to right, was obtained with decreasing catalyst. The lower two frames illustrate alternative views of the case obtained with the lower catalyst level, illustrating the front arrested prior to reaching the bottom of the vial (left) and prior to reaching the outer radius of the vial (right).

AOT/IPDI (in 30/70 weight ratio). This composition is indicated by the “X” in Figure 1 and corresponds to a slight molar excess of PG (20.1% w/w relative to PG–IPDI). Since the phase diagram was prepared at room temperature, we wanted to initially examine polymerization in a similar temperature range, so we added dibutyltin dilaurate at 0.1, 1, and 10 wt % of the PG used in the microemulsions. Although these PG suspensions of the catalyst were not solutions, as soon as these suspensions were added to the corresponding AOT/IPDI solution, the catalyst dissolved.

We initially prepared these microemulsion samples in 20 mL vials. To our surprise we found that this approach resulted in an easily identifiable frontal polymerization process. After an induction period that varied inversely with catalyst amount, a phase transformation seemed to occur at the liquid/air interface within the vials, and then this front steadily migrated toward the bottom of the vial. An excessive amount of heat was generated in the two highest catalyst cases, and an interesting intermediate result was obtained in the case with the lowest catalyst level. These vials, after polymerization, are pictured in Figure 2. The opacity comes from some kind of microphase separation of the surfactant induced by the high heat liberated. We see in the right side of Figure 2 (top) that the frontal propagation in the lowest catalyst level example did not entirely propagate radially to the outer perimeter of the vials, nor did it propagate to the bottom of the vial. This suggested a spatial dimension over which the heat generated during polymerization could be satisfactorily dissipated by conduction to the laboratory air without forcing microphase separation of the surfactant. Magnified side and bottom views of this lowest catalyst level case are shown in Figure 2 (bottom). We subsequently shifted our polymerizations to using culture tubes and

low catalyst levels to control the heat effects. We repeated polymerizations at the same compositions as used for the samples pictured in Figure 2, but in culture tubes (~8 mm i.d.), and indeed we obtained clear polyurethane at the lowest catalyst level.

As an additional control, we also attempted to polymerize the same PG/IPDI ratio as detailed above at the "X" in Figure 1, but instead of the 15% AOT (relative to IPDI) level, we used only a 1% AOT level. Again we used catalyst at 0.1% (w/w) of the PG. This composition corresponds to a position in the multiphase emulsion domain 2 illustrated by the "+". This mixture was emulsified by vigorous stirring and put aside at room temperature. The emulsion, though stabilized by a respectable amount of surfactant, AOT, broke, and the PG and IPDI phases separated without any appreciable reaction.

Molecular weight analyses of the polymerization product (at point "X" in Figure 1 with 0.1% catalyst) by gel permeation chromatography indicated we got a number-average molecular weight of 1020 (which corresponds to about 3.5 monomer pairs) and a weight-average molecular weight of 5660 (~19 monomer pairs). Using established molecular weight models for A-A + B-B types of addition polymerizations, we can estimate that we obtained a conversion of approximately 63% before solidification of the nanocomposite system restricted further reaction. The optical transparency maintained at lower reaction temperatures indicates the capture of nanostructure, although the bulk of the monomers has been transformed into polyurethane.

Various applications are envisioned for such systems. From a preparative perspective, the polymers obtained represent a facile approach to preparing polyurethane prepolymers. Compositional shifts toward lower PG content will yield isocyanate-capped prepolymers, and shifts to higher PG will yield hydroxyl-capped prepolymers.

Ignition tests (placing polymer in a Fisher burner) showed that these test samples were much more resistant to ignition than the samples prepared by steady emulsification. This fire resistance is substantially due to the inherent fire resistance of AOT that derives from the salt nature of AOT. Preliminary experiments have shown that similar microemulsions coformulated with water (PG/water mole ratio of 1/2) produced closed cell foams that are even more fire resistant.

We hypothesize that the autoignition that led to the frontal polymerization is caused by preferential adsorption of the catalyst, dibutyltin dilaurate, to the microemulsion-air interface. The laurate chains would be expected to impart surface activity, particularly since the catalyst has very limited solubility in PG. Fiori et al.²⁰ only recently reported the first synthesis of polyurethane by frontal polymerization. While the same catalyst was used as in their study, DMSO (at 18% w/w or greater) was used as solvent to cosolubilize the 1,6-hexamethylene diisocyanate and the ethylene glycol. A soldering iron was used to effect ignition. These workers added pyrocatechol to inhibit the catalyst at room

temperature and noted that otherwise combinations of frontal polymerization and spontaneous polymerization occurred in the absence of inhibition.

There are many compositional paths that simply connect the monomer corners with one another, and as mentioned above irregular bicontinuous microstructure must necessarily exist at compositions corresponding to equivalent volumes of PG and IPDI. It will be advantageous to learn how to capture such nanostructure, after polymerization, to learn to produce nanoporous polyurethane coatings for new applications. More extensive studies will be reported shortly.

Acknowledgment. Ms. Michelle Bruck of the Chemir Analytical Services kindly provided the molecular weight distribution data. This work was partially supported by a Spring/Summer Research Award to J.T. from Eastern Michigan University and partially supported by U.S. Army Tank-Automotive and Armaments Command Contract DAAE07-03-Q.

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MA049392A