An Examination of the Gelation of Methacrylate Type Crosslinking Agents for the Preparation of Polymer Monolith with 3D Ordered Network Structures

Hiroshi Aoki, Takuya Kubo, Yoshiyuki Watabe, Nobuo Tanaka, Tomohisa Norisuye, Ken Hosoya,* and Kuniaki Shimbo†
Department of Polymer Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, 606-8585
†*Production & Technology Control Department, Speciality Chemicals Division, Showa Denko K.K., Ogimachi, Kawasaki-ku, Kawasaki, 210-0867*

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The gelation of dimethacrylate type crosslinking agents was studied from the perspective of formation of ordered three dimensional (3D) network structures. Dynamic light scattering (DLS) data showed that the gelation of hydrophilic crosslinking agents having OH groups such as glycerol dimethacrylate (GDMA) was enhanced through hydrogen bonding in a hydrophobic solvent system such as toluene, which afforded more ordered 3D structures.

Conventionally, silica- or polymer-based separation media for liquid chromatography has been used in a particulate shape. In principle, the particle size of the media should be reduced to gain separation efficiency. The smaller size of the particles presumably results in higher packing density in a column, while the column pressure drop of mobile phase transport should be excessively increased. The porosity of a densely packed column with smaller particles may become less than 0.4. Therefore, monolithic type separation media, which is based on in-situ polymerization in a column, has been extensively studied, including polymer-based materials, especially by Svec, et al.[1–3] The polymer monoliths are now mainly prepared with free radical polymerization initiated thermally or through ultraviolet light. The pores of monolithic type media are required to range from mesopores (nm-size) closely related to molecular recognition sites to macro throughpores (μm-size) for mobile phase transport. However, those initiation systems tend to form rather agglomerated, globular network structures. Therefore, it is important to analyze the gelation or phase separation processes of crosslinking agents or both as well as the resultant gel morphology in terms of "tailored 3D networks." In view of this objective, our study focused on the fundamental analysis of the gelation and the phase separation processes of dimethacrylate type crosslinking agents. The study particularly centered on a hydrophilic glycerol dimethacrylate (GDMA) with an OH group in the middle of the structure. Because of this OH group, the hydrophobic interaction between GDMA gels and the solutes such as PAHs (polycyclic aromatic hydrocarbons) is not too high compared to the conventional polymeric solid phase such as poly(styrene-divinylbenzene). This is expected to reduce the peak broadening of PAHs.[4] The chemical modification to GDMA gels can be easily done through this OH in the middle.[5] Moreover, OH is expected to play an important role in physical crosslinking at the early stage of GDMA gelation. Therefore, our measurements were extensively covered by dynamic light scattering (DLS) and CCD (charge coupled device) camera for real time observation as well as SEM, BET, and FT-IR. These results were compared with those of hydrophobic dimethacrylate type crosslinking agents such as ethylene glycol dimethacrylate (EDMA) or 1,6-hexanediol dimethacrylate (HDMA) to elucidate the gelation mechanism of this useful crosslinking agent, GDMA.

Our experiment is now described in detail. Dimethacrylate type crosslinking agents were all commercially available. GDMA was used as it was. EDMA and HDMA were distilled just before use. The initiator used in this work was mainly 2,2′-azobis(iso-butyronitrile) (AIBN). However, 2,2′-azobis(2,4-dimethylvarelonitrile) (ADVN) was used in the case of GDMA/cyclohexanol system because of higher solubility and efficiency. The diluents used were toluene, toluene/methanol (95/5, v/v), and cyclohexanol. A crosslinking agent (2 mL) was added to a diluent (2 mL) solution containing an initiator (6–10 mg) except in the following case: GDMA (0.4 mL) was addede to cyclohexanol (3.6 mL) in order to control the gelation speed within the DLS sensor response. The mixture was filtered through 0.2-μm PTFE filter (DISMIC-25JP; ADVANTEC TOYO) mounted to a syringe (5 mL; B. Braun Melsungen AG) and poured into a test tube. Then, the solution was bubbled with argon gas through a Pasteur pipette for 10 min. The gelation of GDMA, EDMA, or HDMA in toluene (50/50, v/v) was monitored in the test tube mounted in a transparent water bath with CCD camera. In addition, DLS apparatus (ALV5000; He–Ne laser; output; 22 mW; wave length; 632.8 nm; ALV, Langen, Germany) was used for the real time observation of the gelation process. The temperature of DLS sample holder was kept at 60 °C (or 40 °C for GDMA/cyclohexanol) in a water bath and the test tube was set in the holder. The intensity of light scattering was continuously monitored at 90 degree to the incident beam and was analyzed every 30 s through a time resolved method to get the autocorrelation functions of the crosslinking agent systems.[6,7] The gelation process was analyzed by plotting the autocorrelation of scattering intensity vs the relaxation time (autocorrelation curve). Before the beginning of gelation, the autocorrelation curve showed a sharp (rapid) decay reflecting the fluid-like state. In contrast, as the gel point was closer, the autocorrelation began to show a gentle decay (delayed relaxation) because the system became solid-like.

Therefore, the gel point was determined as the moment at which the shape of the autocorrelation curve suddenly changed and showed the most delayed relaxation before the quenching of a gel system. The autocorrelation curves around the gel point of GDMA/ toluene system is shown in Figure 1.

In the next step, the characterization of GDMA gels was made. The gels were washed with THF and dried at 65 °C for 24 h, and gold was deposited on them for SEM observation (Hitachi S-3000N: ×1000–5000). Mesopore measurement of gels was also made with BET method (GEMINI II; micromet-

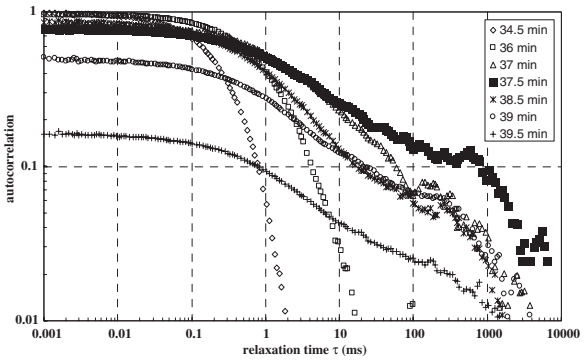

Figure 1. Autocorrelation curves around gel point (37.5 min) of GDMA/toluene system at 60 °C , GDMA/toluene (50/50, v/v).

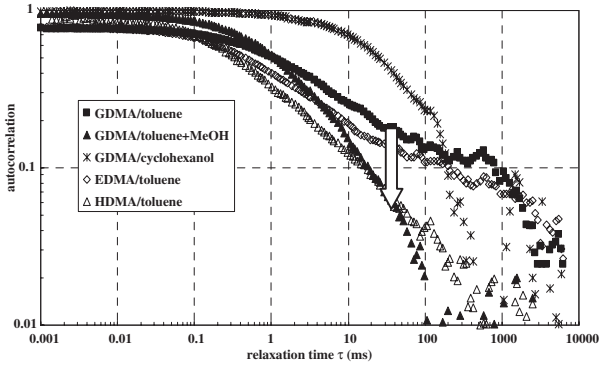

Figure 2. The comparison of DLS autocorrelation curves around gel point of dimethacrylate type cross-linkers at 60 °C, crosslinker/diluent (50/50, v/v) except GDMA/cyclohexanol (10/90, v/v).

rics, USA) to get pore volume and specific surface area. IR zoomed spectrum around 3600 cm^{-1} corresponding to OH was taken with KBr tablets using FT-IR spectrophotometer (JASCO FT-IR/5000).

Then, the results were summarized as follows: Firstly, according to CCD observation, GDMA gel grew intermittently from the bottom of the test tube, whereas those of EDMA gel and HDMA gel grew continuously. This suggested that the GDMA gel growth in toluene might proceed through a repeated process of agglomeration of polymer radicals owing to faster gelation and stepwise phase separation. Secondly, according to the DLS analysis, GDMA/toluene system showed the most delayed relaxation at the gel point, whereas it was accelerated with the addition of methanol. The similar acceleration of the delayed relaxation was observed with the gelation of GDMA in cyclohexanol, an alcoholic solvent. This indicated that the initial gelation of GDMA in toluene might proceed through a strong inter and intra molecular interaction through hydrogen bonding. Relevant DLS data is shown in Figure 2. Thirdly, FT-IR spectrum of GDMA/toluene gel showed an apparently different peak around 3600 cm^{-1} compared with those of the alcoholic systems such as

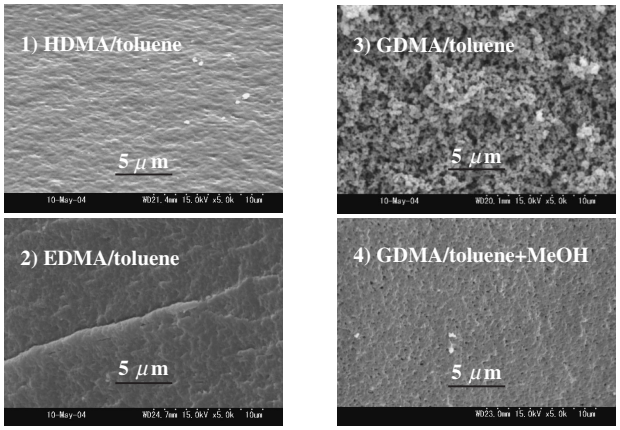

Figure 3. SEM picture of dimethacrylate gels (×5000), crosslinker/toluene (50/50, v/v) system polymerized at 60 °C, 5% methanol added to toluene (5/95,v/v) in image 4).

GDMA/(toluene added with 5% methanol) and GDMA/cyclohexanol. This strongly suggested the large possibility of the hydrogen bonding based on OH of GDMA gel formed in GDMA/toluene system. The SEM pictures shown in Figure 3 indicated that the unique macroporous feature of GDMA gel was formed in GDMA/toluene system with μm-sized pores homogeneously dispersed. In contrast, the gels from HDMA/toluene or EDMA/toluene systems didn't show any macroporous feature. The gel from GDMA/toluene added with 5% methanol showed a rather planar surface with fewer macropores. BET data supported the macroporous feature of the GDMA/toluene gel with the smaller nanopore density.

In conclusion, our analysis indicated that hydrogen bonding restricted the initial linear growing of polymer chains of GDMA in a hydrophobic solvent such as toluene. The hydrogen bonding thus suppressed the piled up 2D networks, and formed the well controlled 3D ordered network structure having both mesopores and throughpores.

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