

Oligomer Viscosity Considerations

Combined Effects of Hydrogen Bonding and Molecular Weight



While a broad range of inter- or intra-molecular forces can influence the viscosity of oligomeric materials, two major forces can have significant impact: the overall molecular weight of the oligomer, and the presence of polar groups within their chemical structure that contribute to intermolecular forces, one type of which is hydrogen bonding. While it is commonly understood that higher molecular weight theoretically correlates with increased viscosity, low molecular weight materials with polar groups that cause significant hydrogen bonding (H-bonding) can often have unexpected viscosity profiles.

Main Viscosity Drivers in Urethane (Meth)acrylate Oligomers

| | Hydrogen Bonding | Molecular Weight (MW) |
|------------------------------|---|---|
| Structure/Property Variables | <ul style="list-style-type: none">Hydroxyl-, Amine- or Carbamate (urethane) groupsDegree of polarityPolar group density | <ul style="list-style-type: none">High vs Low Molecular weightLinear vs branched vs hyper-branchedMolecular weight distribution |
| Effect on viscosity | Strong polar groups form intermolecular attractions, increasing the resistance to flow | Higher molecular weight increases physical entanglement, impeding molecular movement |

Figure 1 describes the undiluted viscosities of a range of oligomeric materials whose only significant difference between them is the increasing molecular weight of the polyol soft segment chain in the material.

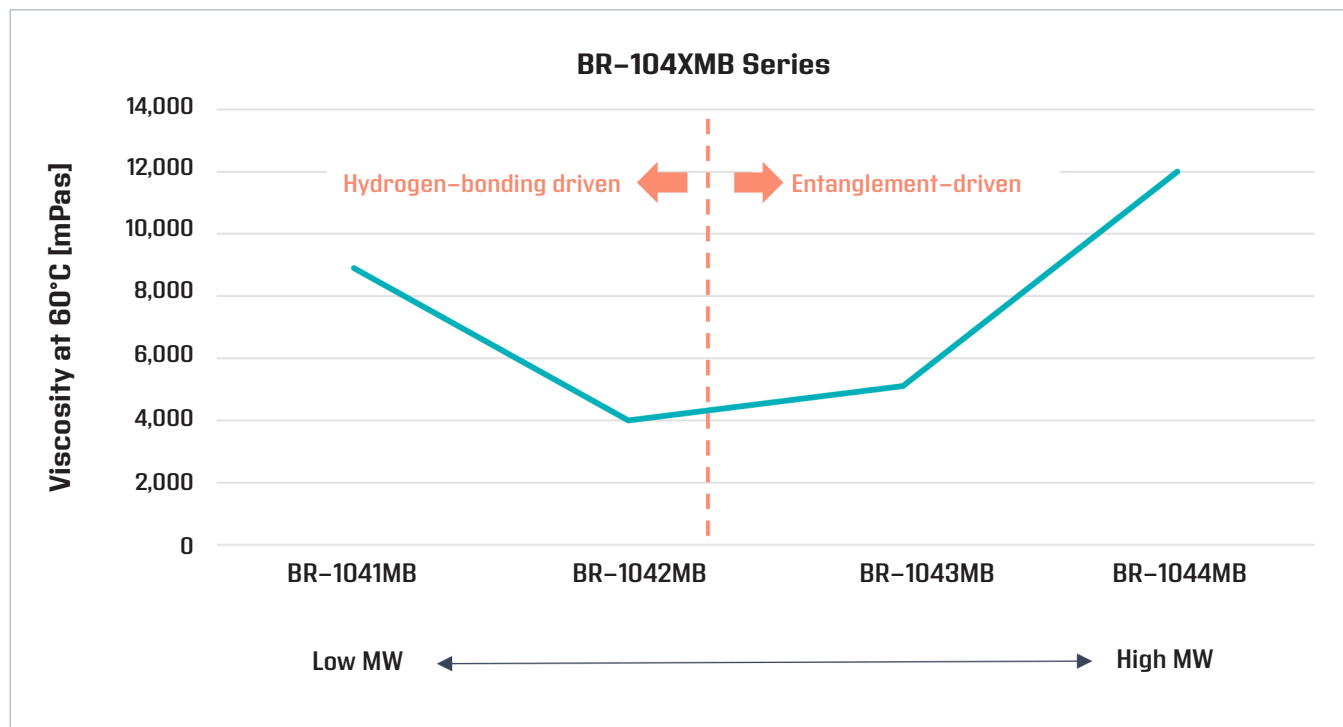


Figure 1. Example of the influence of hydrogen bonding and entanglement on the viscosity of polyether-based urethane methacrylate oligomers with varying molecular weights: Bomar bio-based oligomers series BR-104xMB

A theoretically reasonable explanation for this U-shaped graph would be that the dominating driver of viscosity within the bulk material shifts from H-bond forces in the low MW materials (BR-1041MB, BR-1042MB) over to entanglement forces in the higher molecular weights (BR-1043MB, BR-1044MB). The sum of both effects reaches a minimum somewhere between the medium MW materials (BR-1042MB and BR-1043MB), where both forces have their minimum contribution to the overall viscosity of the material. At low MW it is theorized, the increased H-bond density contributes to a much higher than expected viscosity than if one were to only consider the MW of the material alone.

These forces not only play an important role on polymeric materials in their neat state, but also in their diluted state, which is arguably a more important consideration. Oligomers with significant H-bonding will often have a very high viscosity in the undiluted form, but as additional diluents are added to the product, the material will “let down” very rapidly to result in a relatively low viscosity final formula.

For example, when diluted in a non-polar monomer such as HDDA, BR-1044MB (high MW) has a lower viscosity at 10% HDDA compared to the same dilution of BR-1041MB (low MW). At this dilution, the higher H-bond density in the BR-1041MB creates more resistance to flow compared to the entanglement-driven forces in the BR-1044MB. However, as the oligomers are increasingly diluted and the H-bond density decreases, entanglement increasingly dominates the effects of viscosity (see Figure 2).

BR-1041MB vs BR-1044MB

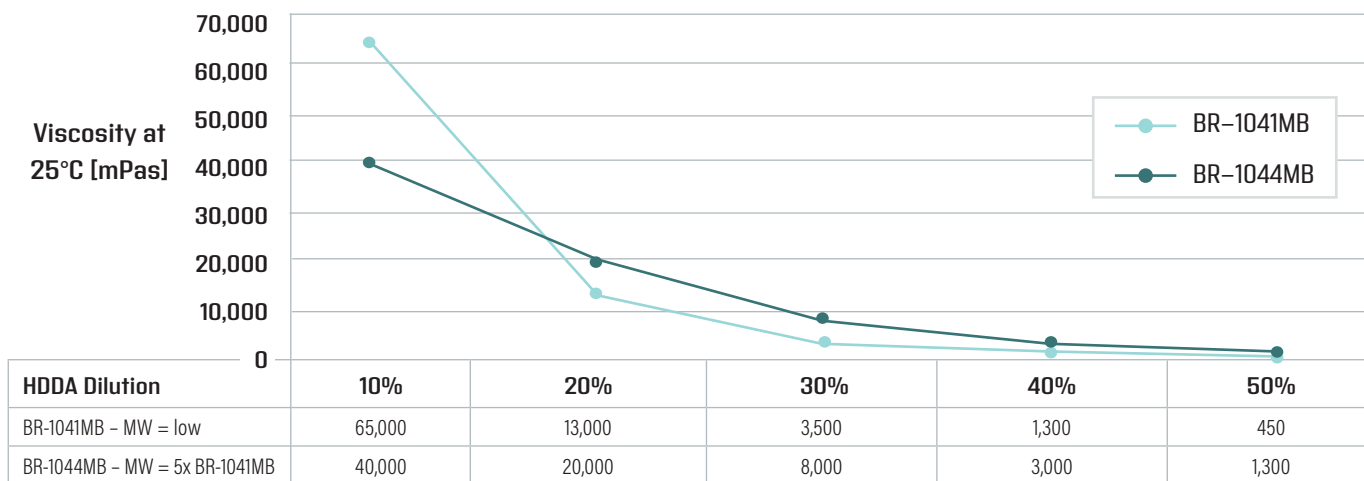


Figure 2. Dilution behavior of polyether based urethane methacrylate oligomers with different molecular weights

This unexpected viscosity reduction trend can be observed across different polymer compositions, as additionally demonstrated on the polyester-based urethane acrylate oligomers BR-741 (low MW) and BR-7432GB (high MW) in Figure 3. Both oligomers consist of a very similar chemical structure but have significantly different relative molecular weights with an approximate factor of 7.

BR-741 vs BR-7432GB

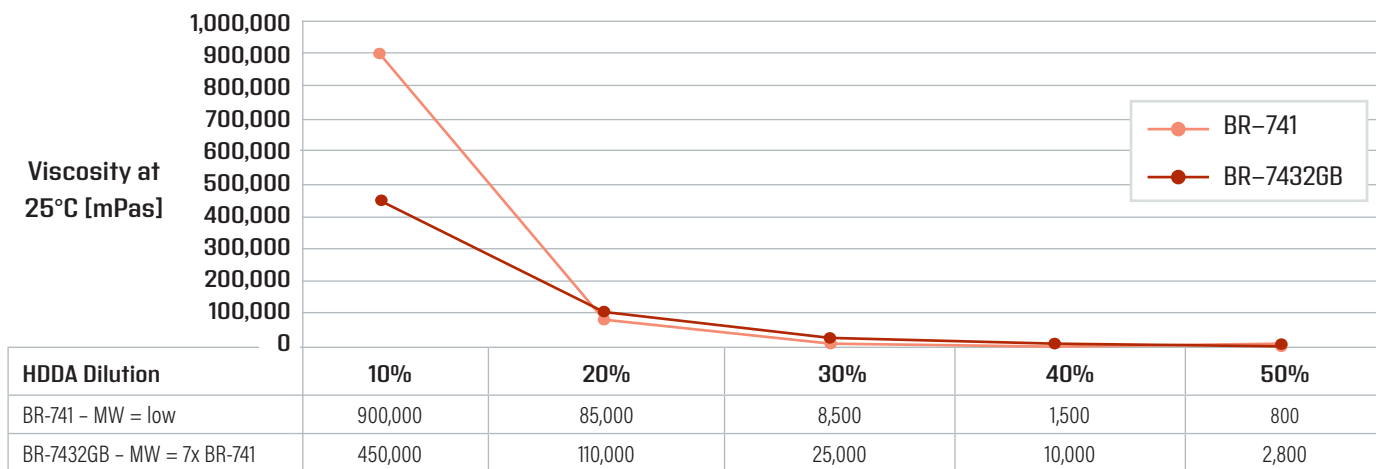


Figure 3. Dilution behavior of polyester-based urethane acrylate oligomers with different molecular weights

Understanding how molecular weight and polar groups affect viscosity and dilution behavior is essential for formulating coatings, adhesives, and other materials where control over flow properties and compatibility with solvents is crucial. Low molecular weight, high H-bond density materials can also be considered for use in applications requiring a low final viscosity once the dilution profile of the material is understood. By carefully selecting oligomers with specific molecular weights, polar group concentrations and dilution rates, formulators can achieve desired viscosity profiles and tailor the product behavior to meet specific application requirements.

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