Communications to the Editor

Effect of Dipole Moment on the Maximum Rate of Photoinitiated Acrylate Polymerizations

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Photoinitiated polymerization of methacrylates and acrylates is one of the most efficient processes for the rapid production of polymeric materials with well-defined properties and is widely employed in high-performance inks, coatings, stereo-lithography, dental restorative fillers, and the preparation of contact lenses.[1,2] These applications drive the need to develop a better understanding of these bulk polymerizations. Photo-DSC[3] was initially employed to monitor real-time acrylate conversions calorimetrically. High-speed real-time kinetic data could only be obtained after the pioneering work of Decker, who developed real-time infrared spectroscopy (RT-IR) in which the need for the enthalphy of polymerization was eliminated.[4] To date, both techniques are well established,[5] and based on the results obtained, a wide variety of kinetic models has evolved.[6]

As far as we are aware, the understanding of different acrylate reactivities in relation to their molecular structure has received little or no attention. Generally the photoinitiator (or mixture thereof) has been altered to obtain higher reaction rates. Andrzejewska et al. reported a heteroatom effect,[7] and Guymon et al. found rate enhancements in liquid crystalline phases.[8] Decker et al. reported on new acrylates with a high intrinsic reactivity.[9] Although no explanation was given on a molecular level for the observed high intrinsic reactivity, this work triggered our research to evaluate different acrylates reactivities in term of hydrogen-bonding capability,[10] one of nature's dominating organizational tools. The influence of hydrogen bonding on polymerization rate was confirmed by Bowman.[11] In this communication we present our data on acrylates that are not capable of hydrogen bonding and discuss the results in terms of dipolar interactions.

One of the difficulties faced in discussing acrylate reactivity in terms of dipolar interactions is the fact that for most of the interesting highly reactive monomers the dipoles are unknown. Although the dipole moment of an energy-minimized structure could give an indicative value, it has to be realized that in a (neat) solution more conformations than just the minimum-energy structure are present and that the average dipole moment could differ significantly from the dipole of the energy-minimized structure. Therefore, we calculated the dipoles as the Boltzmann-averaged dipole moment.[12]

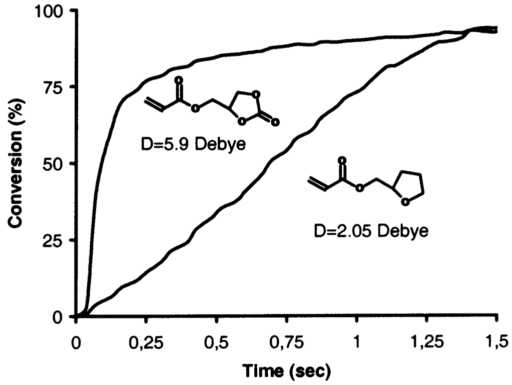

Figure 1. RT-FTIR time−conversion plots of acrylates with a high and low calculated dipole moment.

RT-FTIR[13] using a large-angle transmission reflection cell with inerting and temperature control was used to monitor these fast acrylate conversions under UV irradiation (intensity 135 mW/cm^2) in a nitrogen atmosphere. Differentiation afforded the maximum rates of acrylate polymerization.[14] All final conversions, i.e., after 15 s irradiation, were above 98%. The monomers were prepared by reacting acryloyl chloride with the corresponding alcohols. The products were distilled at least three times before use (purity >99% based on GC). Hydroxy cyclohexyl phenyl ketone (1%) (Irgacure 184) was employed as photoinitiator. Representative plots of two acrylates with different polarity are shown in Figure 1.

The results of this study between polarity and rate of polymerization are shown in Table 1 and Figure 2 (black diamonds). These results suggest that, at least for dipole moment values above 3 D, a direct correlation between the maximum rate of polymerization and the dipole of an acrylate monomer exists. This correlation between a molecular characteristic/property (dipole moment) and the maximum rate of acrylate polymerization facilitates, for the first time, the rational design of new monomers with an enhanced reactivity instead of the trial and error approach applied so far.

Acknowledging that the Boltzmann-averaged dipole moment is the rate-determining factor, then under identical conditions mixtures of acrylate monomers should exhibit the same behavior. To prove this relationship between the dipole moment and the maximum polymerization rate, we examined various mixtures of tetrahydrofurfuryl acrylate ($D = 2.05$ D) and oxazolidone-*N*-ethyl acrylate ($D = 5.3$ D). The results obtained (Figure 2, open circles) were in line with the expectations, confirming that the dipole moment−maximum polymerization rate relationship holds for neat monomers as well as mixtures of monomers.

The correlation between dipole moment and maximum rate can be explored further as it appeared to be valid in the presence of small amounts of inert solvents.

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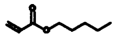
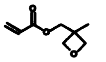
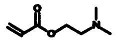
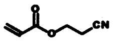
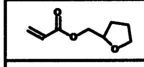
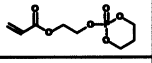
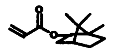
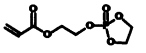
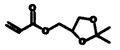
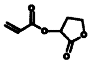
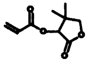
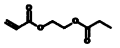
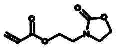
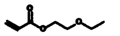
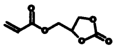
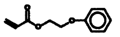
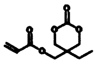
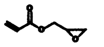
Table 1. Calculated Boltzmann-Averaged Dipole Moment and the Maximum Rate of Polymerization of Acrylate Monomers

Compound	Dipole	Rate	Compound	Dipole	Rate
	1.8	2.2		2.65	8.2
	2.01	1.04		3.7	13.9
	2.05	5.3		3.87	17.8
	2.08	5.83		4.12	17.9
	2.17	7		4.54	18.4
	2.24	2.1		4.62	21.7
	2.4	3.95		5.3	27.3
	2.42	2.67		5.92	29.9
	2.49	4.12		6.5	33
	2.59	4.11			

[a] Dipole moments in debye and rates in mol/(L s).

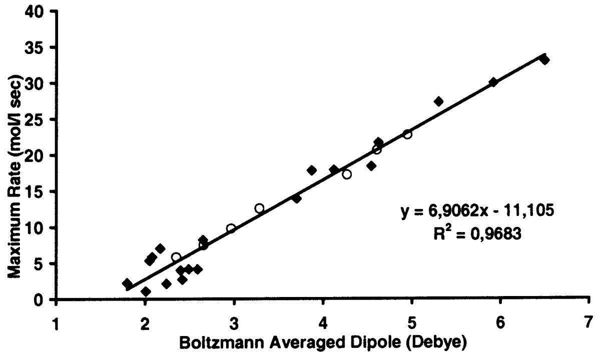


Figure 2. Relationship between maximum rate of photoinitiated acrylate polymerization and the calculated Boltzmann-averaged dipole moment: black triangles, pure monomers; open circles, mixtures of tetrahydrofurfuryl acrylate and oxazolidone-*N*-ethyl acrylate.

In Figure 3 the effect of diluting tetrahydrofurfuryl acrylate with a highly polar solvent (propylene carbonate, $D = 5$ D) or with a lower dipolar solvent (dimethyl carbonate, $D = 0.9$ D) solvent is shown. To minimize evaporation of the solvents, the experiments were performed as laminates. This alternative sampling arrangement affects the light intensity and sample thickness, which results in different rates and consequently a different correlation, though the basic dipole moment—maximum polymerization rate relation is still observed. The rates of neat tetrahydrofurfuryl acrylate are indicative for these changes as 5.3 mol/(L s) is found in the transmission reflection setup vs 3 mol/(L s) in the transmission setup. It should be noted that the correlation found in the dilution experiments with inert solvents is only valid as long as the bulk of the solution is the acrylate monomer (up to 30% inert solvents). However, this very feature enables rate enhancements via the addition of small amount of an inert solvent, which is contrary to the general belief that dilution automatically leads to reductions in polymerization rate.

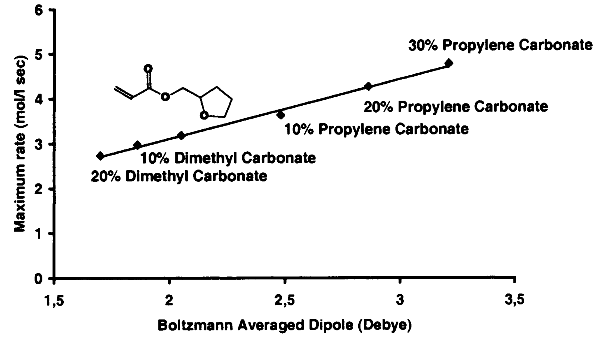


Figure 3. Relationship between maximum rate of photoinitiated acrylate polymerization of tetrahydrofurfuryl acrylate, diluted with dimethyl carbonate or propylene carbonate, and the calculated Boltzmann-averaged dipole moment.

In summary, we have demonstrated the direct correlation between the calculated Boltzmann-averaged dipole moment and the measured maximum rate of polymerization, which offers a tool for the rational design of inherently reactive monomers.

To understand these results, several potential explanations can be envisaged. (a) The photoinitiator effectiveness is increased, leading to more propagating radicals. (b) The activation energy of propagation is lowered, leading to a faster propagation. (c) Hydrogen abstraction reactions leading to cross-link points and subsequent faster polymerization (Tromsdorff effect). (d) In a higher dipole medium, i.e., a medium with a higher dielectric constant, the propagating radical is charged to a greater extent, resulting in less termination. (e) A stronger solvent cage is formed at higher dipoles, resulting in a lower termination reaction rate and subsequent faster polymerization.

None of these explanations can be eliminated completely on the basis of the evidence so far. However, considering the dilution experiments in particular, we believe that a combination of the latter two explanations points to the actual mechanism.

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References and Notes

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(12) The Boltzmann-averaged dipole moment for an acrylate monomer is calculated as follows. A set of starting configurations is generated by considering all possible bond rotations using the Discover 95 program. All these configurations are then minimized at the AM1 level using MOPAC 6.0 with the convergence criterion for the maximum gradient (GNORM) set to 0.05. The resulting structures are then sorted by energy, and only the unique structures are retained. A structure is unique when both the energy of formation (>0.01 kcal/mol) and their dipole moment differ (>0.2 D) The Boltzmann-weighted dipole moment is consequently evaluated as $\langle D\rangle = \sum_{\mathrm{j}} D_j(\mathrm{e}^{-\Delta H_j/RT}/\sum_i \mathrm{e}^{-\Delta H_i/RT}) = \sum_j D_j p_j$, with D_j = dipole moment of conformation j, ΔH_j = difference between the heat of formation of conformation j and the heat of formation of the global minimum conformation, T = absolute temperature, and R = Boltzmann constant. p_j = probability of finding the molecule in conformation j at temperature T. T is set to 298.15 K. The summation over j runs over all unique structures. Sorting of structures, retaining only the unique ones, and the calculation of $\langle D\rangle$ is done by means of a FORTRAN program developed by us.

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(14) Spectroscopic monitoring by RT-FTIR was used in preference to calorimetry (photo-DSC) in order to avoid problems like limits time resolution due to the thermal lag (heat transfer) and acknowledging that the heats of polymerization could vary with the different acrylates, thereby introducing uncertainty about the extent of acrylate conversions. This could be due to changes in tacticity as shown in our previous study (ref 10). However, some of the results were verified by photo-DSC using low UV light intensity and 0.1% photoinitiator and where a similar relationship was found.

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