Macromolecules

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Localization of Critical Molar Ratio Intervals for Highly Branched Step-Growth Michael Addition Networks

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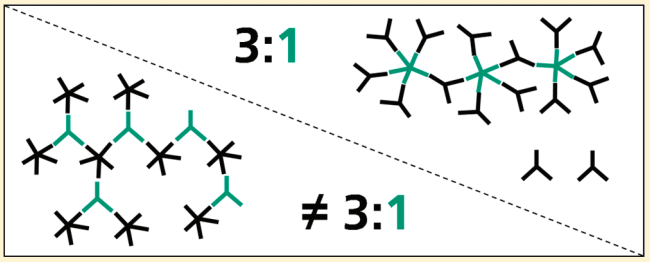
ABSTRACT: Experimental stoichiometric gelation boundaries of a set of branched thiol to acrylate Michael addition polymerization systems were investigated, and the observed limits were compared to theoretical critical molar ratio (CMR) intervals. These CMR intervals were calculated via the Flory–Stockmayer equation (for the upper limit) and via a formula derived from the Carothers equation (for the lower limit). The method provides a simple procedure to verify the existence of a step-growth mechanism in cross-linked polymerizations, and it is also applicable to monomers with functionality distributions. It is shown that the investigated Michael addition systems have gelation boundary values which are consistent with a predominant step-growth mechanism.



INTRODUCTION

Michael additions of thiols to acrylates represent a versatile approach to highly branched polymer networks.[1,2] These reactions can be initiated with bases such as tertiary amines, or nucleophiles like primary amines or phosphines, and they allow relatively high yields of thioether product.[3] Many different acrylates and thiols with various functionalities are commercially available. Particularly interesting for any application are low-odor thiols.[4] For that, thiols having an inorganic $[SiO]_x$ backbone can be employed which can be synthesized via hydrolysis and condensation of mercaptosilanes.

The purpose of this paper is the investigation of the stoichiometry-dependent gelation behavior of Michael addition polymerizations of two different thiols to three commercial acrylates and the calculation of corresponding theoretical CMR interval values for comparison.

Because of the step-growth nature of the Michael addition reaction,[3] whose conversion x progresses by definition from 0 to 1, the organically cross-linked systems exhibit a sharply defined gel point at a certain critical extent of reaction x_c. As proposed by Flory,[5] these polymerizations can approximately be described to proceed through reactions of equally reactive, independent functional groups reacting exclusively intermolecular with each other (Flory principle). Stockmayer[6] derived a general simple expression for x_c, applicable to polymerizations which obey the Flory principle, assuming that the weight-average molecular weight M_w becomes infinitely large at the gel point:

$$x_{c,\,St} = \frac{1}{\sqrt{(n_A/n_B)(f_A-1)(f_B-1)}} \qquad (1)$$

Here, n_A and n_B are the moles of reacting functional groups A and B, N_A and N_B represent the moles of monomers bearing A or B groups, and f_A and f_B are the corresponding monomer functionalities. For monomer components with a functionality distribution, the weight-average functionality can be used:

$$f_{avg,\,St} = \frac{\sum_i f_{A/B,i}^2 N_{A/B,i}}{\sum_i f_{A/B,i} N_{A/B,i}} = \frac{\sum_i f_{A/B,i} n_{A/B,i}}{\sum_i n_{A/B,i}} \qquad (2)$$

Expressions for x_c identical to eq 1 were also obtained by Gordon[7] via stochastical cascade processes and vectorial probability generating functions and by Macosko and Miller[8] through recursive probability modeling.

On the basis of eq 1, Dušek et al.[9,10] formulated the critical molar ratio (CMR) for off-stoichiometric mixtures as the excess of groups of one chemical functionality beyond which the system cannot gel, and instead only soluble highly branched polymers are formed:

$$\mathrm{CMR} = \left[\frac{n_A}{n_B}\right]_{crit} = \frac{1}{(f_A-1)(f_B-1)} \qquad (3)$$

These approaches all obey the Flory principle neglecting intramolecular reactions and fluctuating reactivities due to substitution effects. Therefore, the expression for x_c is as a matter of principle slightly too low, and the obtained value for the CMR is slightly too high and is always symmetric for an excess of A or B, irrespective of the corresponding monomer functionality values f_A and f_B. However, since these models are very convenient to use for many applications, and because all attempts to take inequal

Received: April 7, 2011
Revised: May 25, 2011
Published: June 14, 2011

Table 1. Overview of Experimental CMR Values of Michael Addition Networks Expressed as Stoichiometric Proportion Acrylate: Thiol (Acr:SH)

Acr:SH	HDDA		TMPTA		PETA	
TMPTMP	1.5−1.75:1	1:1.5−1.75	3.0−3.5:1	1:2.5−3.0	ca. 5.0:1	1:ca. 3.7
MS	2.5−2.75:1	1:2.75−3.0	4.0−5.0:1	1:ca. 4.0	ca. 7.1:1	1:ca. 5.4

reactivities or cyclizations into account result in immense complications of the mathematical description, these equations remain a feasible approximation.[11]

A different, but very simple, contrarian attempt for an expression for x_c, which, however, has not be considered much, was formulated by Carothers,[12] who applied the number-average molecular weight M_n as the quantity becoming infinitely large at the gel point. This approach was expanded by Pinner[13] for nonstoichiometric monomer mixtures leading to the following equation, when $n_B > n_A$:

$$x_{c,\,Car} = \frac{1}{f_A} + \frac{n_B}{f_B n_A} \qquad (4)$$

Equation 4 overestimates the critical conversion x_c because molecules larger than M_n are present in a polymerizing sample and reach the gel point earlier than those of the size M_n. Therefore, eqs 1 and 4 deliver different theoretical values for x_c which, in combination, provide a very facile theoretical range for experimental values of x_c without the need for numerical calculations.[14]

MATERIALS AND METHODS

The acrylate components pentaerythritol tetraacrylate (PETA, Aldrich, technical grade), trimethylolpropane triacrylate (TMPTA, Cray Valley Atofina, technical grade), and 1,6-hexanediol diacrylate (HDDA, ABCR, purity 99%) as well as trimethylolpropane tris(3-mercaptopropionate) (TMPTMP, Aldrich, purity ≥95%) and triethylamine (TEA, Aldrich, purity ≥99.5%) were used as received. (3-Mercaptopropyl)methyldimethoxysilane (MdiMS, technical grade) was purchased from Shin-Etsu, distilled under reduced pressure, and stored under nitrogen before use to avoid humidity absorption. The purity of MdiMS after distillation was controlled via ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy prior to the hydrolysis/condensation reaction yielding the corresponding mercaptosiloxane.

For the preparation of (3-mercaptopropyl)methylsiloxane (MS), 72.1 g (0.4 mol) of MdiMS was dissolved in 200 mL of ethyl acetate, and subsequently 11.6 mL of 0.5 M hydrochloric acid was added dropwise. After complete reaction, the solution was washed three times with 60 mL of water and dried upon double filtration by means of a hydrophobic filter, and the solvent and the byproduct methanol generated upon synthesis were removed under reduced pressure at 40 °C. Yield: 53.51 g (99.6%). ^{1}H NMR (400 MHz): δ = 0.01−0.11 (m, 3H, $SiCH_3$), 0.56−0.67 (m, 2H, $SiCH_2$), 1.27−1.35 (m, 1H, SH), 1.50−1.70 (m, 2H, CH_2), 2.45−2.51 ppm (m, 2H, CH_2SH). ^{13}C NMR (100 MHz): δ = −0.6 ($SiCH_3$), 16.1 ($SiCH_2$), 27.8, 27.9 ppm (CH_2). ^{29}Si NMR (80 MHz): δ = −23.3−(−22.0) (D^2), −20.8−(−20.3) (D^2 tetrasiloxane), −11.3−(−11.2) (D^1), −9.5−(−9.4) ppm (D^2 trisiloxane).

For inducing Michael addition polymerizations, 20 μL of triethylamine initiator was added to a total amount of 500 mg of an appropriate mixture containing an acrylate and a thiol component in a glass vial. The closed vials were stored at 35 °C for 17 h for complete reaction. Gelled and nongelled samples were discriminated via rheological examination and solubility experiments.

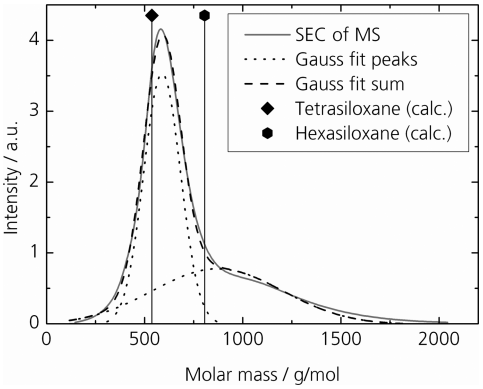


Figure 1. Size exclusion chromatography spectrum (standard: PS) of mercaptosiloxane MS and corresponding Gauss fit peaks and Gauss fit sum for the estimation of the ring size distribution. The calculated values for the tetra- and hexasiloxane are included for comparison.

The NMR spectra were recorded with a Bruker-Spectrospin 400 UltraShield (400 MHz) at 23 °C. Size exclusion chromatography analysis (GPC) was performed at 38 °C using three SDV columns with eluent tetrahydrofuran (1.0 mL/min), with toluene as internal standard and a GAT LCD500 UV 254 nm detector after calibration with polystyrene (PS) standards.

The functionality distributions of the technical grade acrylate monomers were estimated via ^{1}H NMR spectroscopy and that of the mercaptosiloxane (MS) using ^{29}Si NMR spectroscopy and GPC.

RESULTS AND DISCUSSION

The stoichiometry-dependent gelation behavior of Michael addition polymerizations was investigated, using two different thiols, which were employed via Michael addition reaction with three commercial acrylates. The experimental CMR values, which were obtained from triethylamine-induced polymerizations, are presented in Table 1.

Since the commercially available acrylates pentaerythritol tetraacrylate (PETA) and trimethylolpropane triacrylate (TMPTA) were of technical grade, their functionality distributions had to be estimated for the calculation of theoretical CMR values, just as for the synthesized mercaptosiloxane MS. Measurements of solution ^{1}H NMR spectra revealed that the major impurities in TMPTA and PETA were byproducts which result from incomplete acrylation during synthesis; however, the different conceivable byproducts with lower functionality were not discriminable. The corresponding hydroxyl tri- and diacrylate are assumed to be the major byproducts for equilibrium reaction conditions during acrylation. Thus, a comparison of the peak integrals of acrylate, methylene, and hydroxyl protons for PETA and TMPTA provided an opportunity to estimate the composition quantitatively. PETA was determined to contain ∼27% molecules with f_{Acr} = 3, and TMPTA comprised ∼23% diacrylate. Solution ^{29}Si NMR spectra of the synthesized MS showed

dx.doi.org/10.1021/ma200810e |Macromolecules 2011, 44, 5123–5126

low amounts of silanoles and trisiloxane rings besides a high fraction of tetracyclosiloxane and, additionally, larger rings whose exact size cannot be determined via ^{29}Si NMR spectroscopy due to peak overlap. The peaks were assigned by means of refs 15 and 16. Size exclusion chromatography (SEC) measurements with polystyrene (PS) standard indicate a narrow size distribution comprising a major proportion of a species, whose molecular weight equivalent is within the error of the measurement consistent with the calculated value of the tetrasiloxane as well as a second major portion of slightly higher molecular weight.

Thus, the functionality distribution was estimated from both ^{29}Si NMR spectroscopy and GPC, which revealed that the resulting material most probably is composed of tetrasiloxane rings and slightly larger rings such as hexasiloxanes. This is in good agreement to the preferred ring sizes reported in previous investigations of acid-catalyzed hydrolysis and condensation of alkyl alkoxysilanes.[17]

Using these data, it is possible to calculate the weight-average functionality and theoretical CMR value according to Flory[5] and Stockmayer[6] with eqs 2 and 3 for the investigated monomer combinations. The derivation of theoretical CMR intervals requires an extension of the attempt of Carothers[12] and Pinner[13] in order to deduce the CMR lower limit. In contrast to the Flory−Stockmayer approach, the calculated value for the gel point conversion x_c after Carothers and Pinner from eq 4 is always lower, if the excess component bears the higher functionality than the understoichiometric component in a given off-stoichiometric system. This is readily identifiable by a simple rearrangement of eq 4, as $f_A f_B$ is constant for a given system, and $n_B/n_A > 1$ is valid, since B groups are in excess:

$$x_{c,\,Car} = \frac{1}{f_A} + \frac{n_B}{f_B n_A} = \frac{1}{f_A f_B}\left[f_B + \frac{n_B}{n_A} f_A\right] \qquad (5)$$

Similar to the derivation of eq 3 from eq 1, a minimum critical molar ratio (CMR_{min}) is found from eq 4 by defining $x_{c,Car} = 1$ as conversion boundary value:

$$CMR_{min} = \left[\frac{n_B}{n_A}\right]_{crit} = \left(1 - \frac{1}{f_A}\right) f_B = f_B - \frac{f_B}{f_A} \qquad (6)$$

For monomer components having a functionality distribution, here the number-average functionality has to be used (cf. Appendix for formal derivation):

$$f_{avg,\,Car} = \frac{\sum_i f_{A/B,i} N_{A/B,i}}{\sum_i N_{A/B,i}} \qquad (7)$$

The resulting values for CMR_{min} are likewise asymmetric, namely larger for a given off-stoichiometric system as the excess component bears the higher functionality f.

A comparable asymmetry can be illustrated by sketching the maximum intermolecular cluster for simple, asymmetric and off-stoichiometric examples as the one depicted in Figure 2.

Figure 2a shows that it is possible to combine all monomers intermolecularly into one large cluster, whereas this is not possible for the same excess of B:A in Figure 2b. For both hypothetical systems (a) and (b) in Figure 2 the Flory−Stockmayer eq 1 yields the critical conversion $x_{c,St} = 0.61$, irrespective of the fact whether the excess (a) or deficient (b) component bears the higher functionality. In contrast to this, the calculation of x_c with eq 4 yields no possible gelation ($x_c > 1$) for case (b) in Figure 2 and a value $x_{c,Car} = 0.93$ for case (a). Thus, the asymmetry tendency observable among the maximum intermolecular clusters of Figure 2 is well described through eq 4. It is important to note that the concept of a maximum intermolecular cluster is identical with neither the molecular situation at the gel point after the Stockmayer model nor the Carothers model. For the gel point of Figure 2a according to eq 4, exactly one more linkage is required than displayed, namely the first necessarily intramolecular bonding. This can also easily be visualized by a simple modification of eq 4 given in the following, keeping in mind that $n = Nf$ for all reacting functional groups of one kind:

$$x_{c,\,Car} n_A = \frac{n_A}{f_A} + \frac{n_B}{f_B} = N_A + N_B \qquad (8)$$

Thus, it becomes apparent that the gel point according to Carothers draws the theoretical upper line of the Flory principle, which postulates that independent functional groups react exclusively intermolecular with each other. At that degree of conversion, one intermolecular linkage per initial monomer molecule has been formed such that the entire polymerizable material

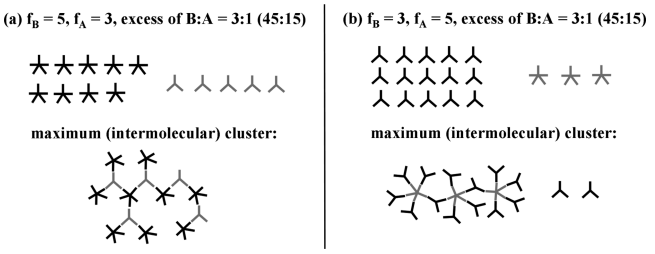


Figure 2. Schematic illustration of intermolecular connective network asymmetry in an off-stoichiometric step-growth system of molecules bearing A groups (gray) and monomers with B groups (black) in excess, where is $f_A \neq f_B$.

Table 2. Overview of Theoretical CMR Values from eqs 3 and 6 Compared to Experimental Results of Michael Addition Networks

Acr:SH			HDDA		TMPTA		PETA	
Carothers		f_{avg}	2		2.77		3.73	
Stockmayer					2.83		3.78	
Carothers	TMPTMP	3	1.3:1	1:1.5	1.8:1	1:1.9	2.5:1	1:2.2
exp result			1.5−1.75:1	1:1.5−1.75	3.0−3.5:1	1:2.5−3.0	ca. 5.0:1	1:ca. 3.7
Stockmayer			2.0:1	1:2.0	3.7:1	1:3.7	5.6:1	1:5.6
Carothers	MS	4.4	1.5:1	1:2.2	2.1:1	1:2.8	2.9:1	1:3.2
exp result			2.5−2.75:1	1:2.75−3.0	4.0−5.0:1	1:ca. 4.0	ca. 7.1:1	1:ca. 5.4
Stockmayer		4.5	3.5:1	1:3.5	6.4:1	1:6.4	9.7:1	1:9.7

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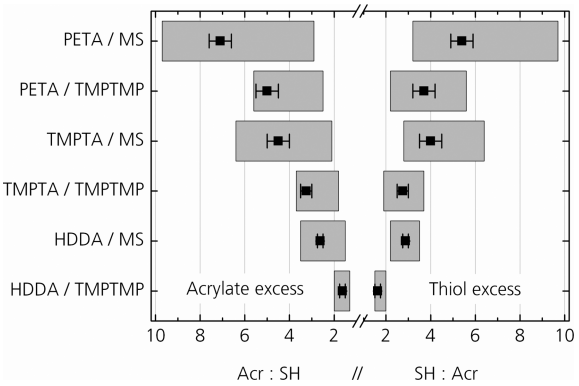

Figure 3. Graphic illustration of theoretical CMR value intervals from eqs 3 and 6 (gray bars) compared to experimental results of Michael addition networks (■).

is bound into one large molecule, and no sol remains for further polymerization reactions.[5]

Using these considerations and the above-described experimental data derived from NMR and GPC measurements, the different average functionalities of the monomer components were calculated with eqs 2 and 7 and the CMR intervals of the systems were determined according to eqs 3 and 6, respectively. Therefore, our experimental gelation results can now be compared with the theoretical predictions (Table 2 and Figure 3).

As obvious from Table 2 and Figure 3, all experimental CMR values are well within the calculated ranges proving sufficient calculation accuracy and good agreement between the combined theories and the experiments. Furthermore, the experimentally determined stoichiometric gelation boundaries are in many cases asymmetric. And for the two cases with significant functionality differences, namely HDDA/MS and PETA/TMPTMP, the tendency of asymmetry is as predicted by calculations using eq 6. However, some asymmetries seem to be more favorable for an acrylate excess instead of the higher functional monomer, for example in the case of PETA/MS. This may be explained by occurrence of minor acrylate homopolymerization after thiolate initiation similar as reported by Reetz and Ostarek,[18] which will be further investigated.

■ CONCLUSION

A series of branched thiol to acrylate Michael addition polymerization systems were investigated in terms of stoichiometric gelation boundaries. The observed limits for gelation ability were compared to theoretical critical molar ratio (CMR) intervals calculated via a combination of the Flory−Stockmayer and Carothers−Pinner gelation equations. For that purpose, a minimal CMR was deduced from the Carothers equation in analogy to the derivation by Stockmayer and Dušek, which is also applicable for monomers of technical grade with a functionality distribution. This method provides a very facile procedure to verify the existence of a step-growth mechanism in cross-linked polymerizations. The approach after Carothers yields additional information about the asymmetric tendency of CMRs for off-stoichiometric systems, when monomer couples of different average functionalities are polymerized. For the investigated Michael addition systems, the obtained boundaries were in good agreement with the calculated CMR intervals though minor changes in asymmetric tendencies suggest a marginal influence of acrylate homopolymerization.

■ APPENDIX

The Carothers equation[12] states that at the gel point the critical conversion x_c is

$$x_{c,\,\mathrm{Car}} = \frac{2}{f_{\mathrm{avg}}} \tag{A1}$$

where f_{avg} is the general number-average functionality:

$$f_{\mathrm{avg}} = \frac{\sum N_i f_i}{\sum N_i} \tag{A2}$$

For a system with N_A molecules bearing A groups and N_B molecules with B groups and an excess amount of B, one can convert eq A2 according to Pinner[13] and write

$$f_{\mathrm{avg}} = \frac{2(N_A f_A)}{N_A + N_B} = \frac{2n_A}{N_A + N_B} = \frac{2(\sum N_{A,i} f_{A,i})}{N_A + N_B} = \frac{2(N_A f_{A,\,\mathrm{avg}})}{N_A + N_B} \tag{A3}$$

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