

Bulk Hydrosilylation Reaction of Poly(dimethylsiloxane) Chains Catalyzed by a Platinum Salt: Effect of the Initial Concentration of Reactive Groups on the Final Extent of Reaction

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ABSTRACT: Model silicone networks obtained by curing linear poly(dimethylsiloxane) (PDMS) chains with end-vinyl groups, (B_2), with a polyfunctional silane-terminated crosslinker of functionality f , (A_f), through a hydrosilylation reaction have been widely used. In these networks, the principal characteristics of their ultimate molecular structure are strongly affected by the final extent of reaction reached during the crosslinking reaction. This work analyzes the effect of the initial concentration of the reactive end groups on the maximum attainable extent of reaction under normal bulk crosslinking conditions. This was accomplished by examining the reaction between linear B_2 PDMS chains with difunctional and trifunctional silanes. The experimental results were fitted by an exponential equation to have an empirical equation able to predict the maximum extent of reaction to be obtained as a function of the initial concentration of reactive groups. Molecular parameters relevant to this study, such as the degree of polymerization, the weight-average molecular weight for the $A_2 + B_2$ system, or the weight fraction of solubles for the $A_3 + B_2$ system, were calculated with a mean field theory (recursive approach). © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 1099–1106, 2003

Keywords: poly(dimethylsiloxane); hydrosilylation reaction; maximum extent of reaction; model networks; networks; polysiloxanes; step-growth polymerization

INTRODUCTION

Fundamental studies of polymeric materials require detailed information of their molecular structure. In the case of elastomeric crosslinked materials, one of the main features of their molecular architecture is the interconnection between the polymeric chains in a three-dimensional macroscopic network.^{1–3} Thus, the synthesis of well-characterized model networks has been

extensively used for the study of relationships between the molecular structure and different physical properties.^{4–8} One of the reactions that has been extensively used for this purpose is the hydrosilylation reaction between vinyl-terminated difunctional poly(dimethylsiloxane)s (PDMS's) and polyfunctional crosslinkers bearing silane groups in the presence of a Pt salt.^{7–10}

The hydrosilylation process involves the addition of a silane group to a multiple bond (generally vinyl or allyl groups). It could be initiated or catalyzed in several ways, metal catalysis being the most common. The catalyst can be metal salts, supported metals, or transition-metal complexes.¹¹

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Although the use of the hydrosilylation reaction for linear polymerization has been known for 45 years, only oligomeric products with low molecular weight could be synthesized by this procedure.^{12,13} The production of ionic compounds as byproducts generated during the reaction is responsible for undesirable reactions. However, recent studies have suggested that the role of the catalyst used for the reaction is very important.¹¹⁻¹³

However, the hydrosilylation reaction has also been widely used to make liquid-crystal polymers, chiral polymers, hyperbranched and dendritic structures, and macromolecules with redox-active centers. One of the advantages of this reaction is its high selectivity, which tolerates many functional groups including esters, nitriles, amines, amides, nitro groups, ketones, ethers, phosphates, sulfides, and sulfones.¹⁴ Several examples of functionalized polymers and novel architectures were described in a brief review of hydrosilylation polymerization by Grate et al.¹¹

Although a wide range of soluble catalysts have been investigated for hydrosilylation reactions, most research and industrial syntheses are carried out in the presence of platinum complexes. Speier's catalyst (hexachloroplatinic acid) is widely used in the commercially important hydrosilylation of unsaturated substrates such as alkenes. Other platinum complexes also exhibit high activity during the curing of polysiloxanes containing vinyl groups, such as Pt(PPh₃)₂Cl₂: *cis*-dichlorobis (triphenylphosphine) platinum (II), PtCl₂(C₂H₄)₂: di- μ -chloro-dichlorobis (ethylene) diplatinum (II), [(PhO)₃P]₄Pt: tetrakis (triphenoxyphosphine) platinum (IV), and *cis*-Pt[(C₂H₅)₂S]₂Cl₂: *cis*-dichlorobis (diethylsulfide) platinum (II), which allow polymerization products of high molecular weight.¹⁵ However, Karstedt's catalyst (2% platinum divinyltetramethyl-disiloxane complex in xylene) is the preferred hydrosilylation catalyst.^{16,17}

An ideal or model network is obtained when the functional groups at the end chains of a prepolymer chain react with different crosslinkers. If the reaction is complete, all the chain ends are jointed to the resulting polymer network. In these conditions, the average chain length between the crosslinking points is the same as the difunctional prepolymer used in the reaction. Furthermore, if the prepolymer chains are generated through a living polymerization process, it is possible to obtain model networks with very uniform chain-length distributions.

Previous studies¹⁸⁻²¹ of the hydrosilylation reaction have indicated that stoichiometrically balanced systems can reach a maximum extent of reaction that depends on the initial concentration of reactive groups. Chaumont et al.¹⁸ investigated the reaction between vinyl-terminated monofunctional polystyrenes and model molecules containing silane groups. Vallés et al.¹⁹ prepared model PDMS networks crosslinked both in bulk and in solution. Villar and Vallés²⁰ tested some of the conditions necessary to obtain model networks. They obtained an empirical relationship between the maximum extent of reaction obtained experimentally (p_{∞}) and the initial concentration of reactive groups in the mixture (expressed as the inverse of molarity, M⁻¹). Previous results have shown that, in dilute systems, the maximum extent of reaction reached experimentally will be lower than the corresponding to an ideal reaction. This causes the presence of pendant and soluble material in the final structure of the network. Furthermore, in these cases the length of the elastically active chains is higher than that of the prepolymer used in the reaction, and their concentration is lower than expected.

To understand the relationship between the final structure of the network and its properties, it is very important to account for all the imperfections generated during the crosslinking process. Consequently, this work analyzes some conditions where model networks can be obtained, and new empirical relationships between the maximum extent of reaction and the initial concentration of reactive groups in the mixture are proposed.

EXPERIMENTAL

Synthesis

The influence of the initial concentration of reactive groups on the maximum extent of reaction was carried out through a linear system (A₂ + B₂) and a network-formation system (A₃ + B₂), such as those depicted in Figure 1(a,b). Commercial PDMS's with vinyl-terminal groups in both ends (B₂) were used (United Chem Technologies). The weight-average molecular weight (M_{wB_2}) of the original prepolymer chains was varied in the range of 10⁴-10⁵ Da. The number-average molecular weight (M_n) was measured by Fourier transform infrared spectroscopy (FTIR) and size exclu-

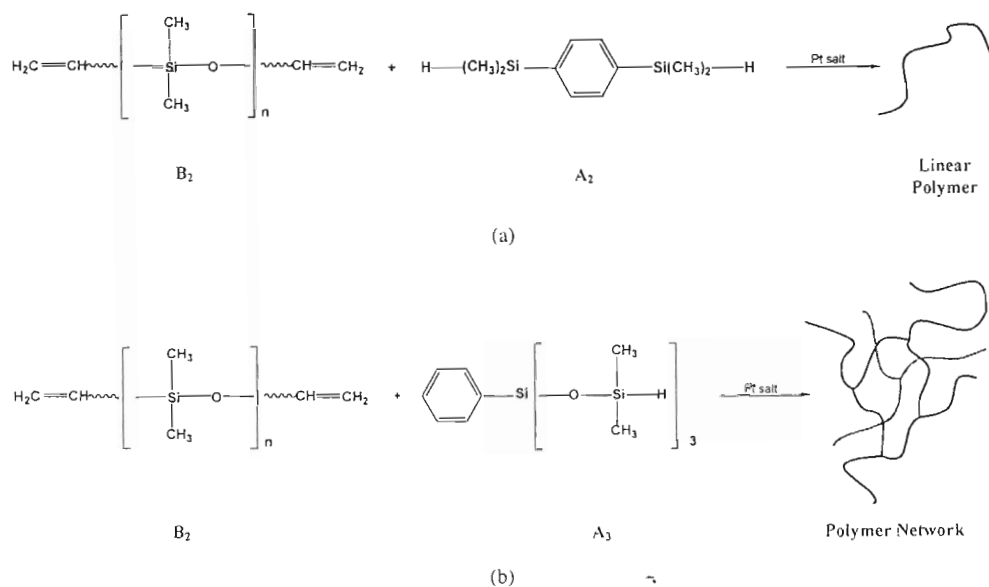


Figure 1. (a) Representation of the linear system ($A_2 + B_2$). (b) Representation of the network-formation system ($A_3 + B_2$).

sion chromatography (SEC) as reported in the literature.²² These results are shown in Table 1.

For the chain-extension reactions *p*-bis(dimethylsilyl) benzene (A_2) was used. The crosslinker used for the network-forming systems was phenyl tris(dimethylsiloxy) silane (A_3). United Chemical Technology provided both reactants. A platinum salt (*cis*-[Pt[(C₂H₅)₂S]₂Cl₂]) was used as hydrosilylation catalyst.

For each one of the B_2 used, reactive mixtures with different stoichiometric imbalances were prepared. The reactants were mechanically stirred and vacuum-degassed to remove the bubbles formed. The hydrosilylation reactions were carried out at 60 °C for approximately 48 h.

Molecular Characterization

Linear polymers obtained by the reaction between $A_2 + B_2$ were molecularly characterized by

SEC at room temperature in a Waters model 440. Toluene was used as the carrier solvent with a flow rate of 1 mL/min. A set of four PLgel columns (500, 10³, 10⁴, and 10⁶ Å) was used. The molecular weight distribution of the reaction products and the M_n and M_w were obtained. The equipment was calibrated with polystyrene (PS) standards of narrow molecular weight distribution (Press Chem Corp.). Benoit's universal calibration²³ was applied. Mark-Houwink's constants for PDMS and PS in toluene at 20 °C were obtained from the literature.²⁴ Values of $K = 4.16 \cdot 10^{-3}$ and $\alpha = 0.788$ for PS and $K = 2.43 \cdot 10^{-3}$ and $\alpha = 0.84$ for PDMS were used.

Rheological Characterization

To compare the values of M_w obtained by SEC, the reaction products of the linear system were also rheologically characterized. This character-

Table 1. Number and Weight-Average Molecular Weights and Polydispersity of the Commercial Linear Poly(Dimethylsiloxane)s Obtained by FTIR and SEC

| Polymer | $M_n \times 10^{-4}$ (Da) FTIR | $M_n \times 10^{-4}$ (Da) SEC | $M_w \times 10^{-4}$ (Da) SEC | M_w/M_n SEC |
|----------------|-----------------------------------|----------------------------------|----------------------------------|------------------|
| D ₁ | 0.53 | 0.50 | 1.19 | 2.38 |
| D ₂ | 0.71 | 0.72 | 2.05 | 2.85 |
| D ₃ | 0.79 | 0.79 | 2.21 | 2.80 |
| D ₄ | 1.89 | 2.25 | 3.58 | 1.60 |
| D ₅ | 3.49 | 3.53 | 5.55 | 1.57 |
| D ₆ | 5.06 | 4.63 | 7.09 | 1.53 |

ization was carried out in a mechanical spectrometer (Rheometrics Dynamic Analyzer RDA-II) in the range of temperatures of 40–140 °C. It was carried out by dynamic tests with parallel plates of 25 mm diameter obtaining the elastic (G') and the loss (G'') moduli with strain amplitudes within the range of linear viscoelasticity. Master curves were obtained with the time-temperature superposition principle to extend the range of measured frequencies. The zero shear rate viscosity (η_0) was obtained from the loss modulus at the low-frequency limit; subsequently it was used to calculate the M_w .²⁵

Weight Fraction of Solubles and Degree of Swelling

The networks obtained from the $A_3 + B_2$ system were characterized by measuring the weight fraction of solubles (W_s) and the volume fraction of polymer in networks swollen with toluene (V_{2m}). The samples were weighed and placed in glass flasks with the solvent to remove the soluble material. The extraction was carried out for 1 month at room temperature, and the solvent was replaced every 3–4 days. After the extraction of solubles, the swollen samples were weighed to obtain the degree of swelling. Then, the samples were vacuum-dried at 40 °C until complete removal of the solvent. They were weighed again, and the weight fraction of soluble material (W_s)

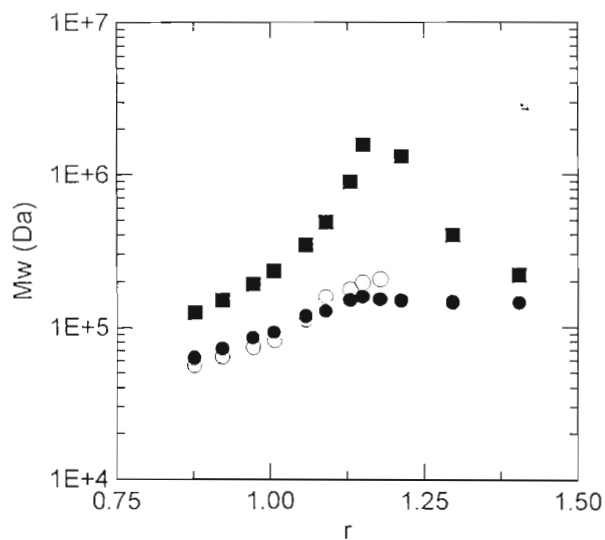


Figure 2. M_w as a function of the stoichiometric imbalance (r) for the PDMS D_3 ($M_w = 22,100$ Da) (United Chemical Technology). Symbols: (■) predicted by the recursive model, (●) SEC, and (○) rheometry.

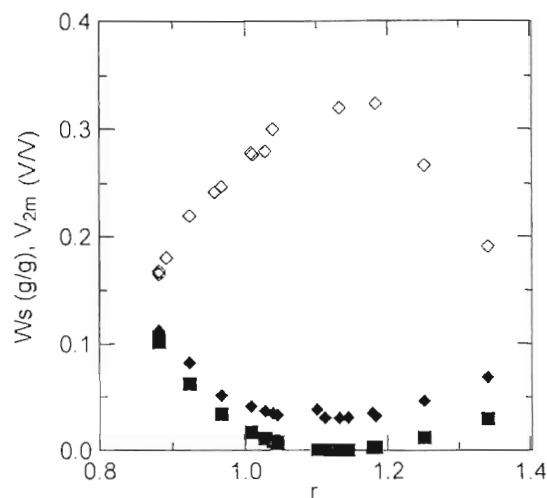


Figure 3. Weight fraction of soluble material (W_s) and volume fraction of polymer in swollen networks (V_{2m}) as a function of the stoichiometric imbalance (r) for the PDMS D_1 ($M_w = 11,900$ Da) (United Chemical Technology). Symbols: (■) W_s predicted by the recursive model, (◆) W_s , and (◇) V_{2m} .

and the equilibrium degree of swelling (V_{2m}) were obtained.

RESULTS AND DISCUSSION

Figure 2 depicts the evolution of M_w of the reaction product of $A_2 + B_2$ ($M_{wB2} = 22,100$ Da). The same behavior was observed for all the prepolymers studied; the maximum extent of reaction was obtained at stoichiometric imbalances higher than one. The evolution of the M_w of a linear system was used to obtain the maximum extent of reaction (p_∞) as a function of stoichiometric imbalance (r). However, the evolution of the weight fraction of solubles and the volume fraction of polymer in the swollen networks for one of the polymer networks is illustrated in Figure 3. These data, obtained from the reaction of the D_1 vinyl-terminated prepolymer chains ($M_w = 11,900$ Da) are representative of those found for all the networks. They exhibit a minimum in the evolution of the W_s with stoichiometry at values of r slightly higher than one. The stoichiometric imbalance r is defined here in the conventional way as the ratio of the initial concentration of silane (A groups) to vinyl (B groups) used in the reaction ($r = [A]/[B]$). A sharp maximum in the fraction of polymer in the swollen networks is observed in the same region, indicating that the highest de-

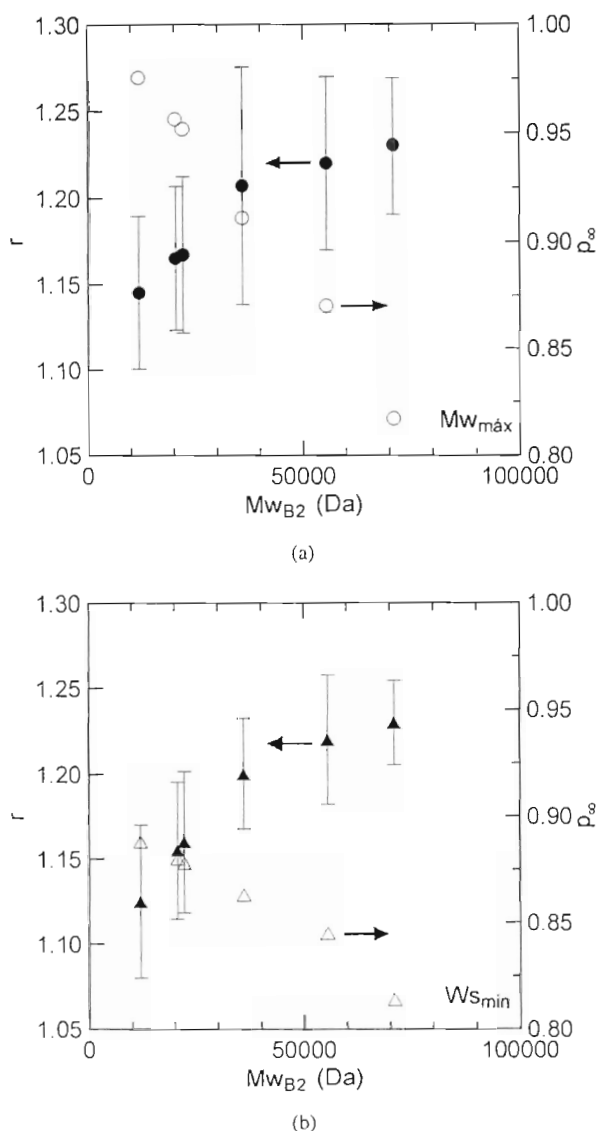


Figure 4. (a) Stoichiometric imbalance (r) for $M_{w\max}$ and final extent of reaction (p_∞) in the system $A_2 + B_2$ as a function of the M_w of B_2 . Symbols: (●) r and (○) p_∞ . (b) Stoichiometric imbalance (r) for $W_{s\min}$ and final extent of reaction (p_∞) in the system $A_3 + B_2$ as a function of the M_w of B_2 . Symbols: (▲) r and (△) p_∞ .

degree of perfection of the networks is attained in all cases with a slight excess of crosslinker. This result can be attributed to a side reaction of crosslinker (A), which could react with itself^{26,27} or because of kinetic limitations preventing the systems, at low r values, to achieve high extents of reaction.²⁸

Figure 4(a) depicts the experimental stoichiometric imbalance (r) for which a maximum final molecular weight ($M_{w\max}$) is obtained for the linear $A_2 + B_2$ case as a function of the M_w of the B_2

prepolymer, M_{wB_2} , that was used in each reaction. The experimental data of M_n or M_w have some uncertainty associated with the characterization technique. For this reason, the value of r for which a maximum molecular weight is obtained ($M_{w\max}$) are reported as the average value of r , where the M_w has a deviation of $\pm 5\%$ of the maximum molecular weight measured experimentally. Therefore, the error bar that corresponds to each case determines the range of the stoichiometric imbalance where it can be found the maximum yield for each of the B_2 prepolymers used in this work. The stoichiometric imbalance for which the maximum yield is obtained increases steadily from values of approximately 1.15–1.23 as the M_w 's of the B_2 prepolymers used in the reaction grow from 11,900 to approximately 55,000 Da. The excess of chain extender necessary to obtain the highest degree of polymerization increases rapidly with the molecular weight of the prepolymers below 50,000 Da and then tends to stabilize in a value of r slightly higher than 1.25.

Figure 4(b) portrays the results of the fraction of solubles extracted from the completely reacted networks, which were prepared by crosslinking the same series of B_2 prepolymers with the trifunctional silane. The plot shows the value of r at which the minimum fraction of solubles was obtained from a series of $A_3 + B_2$ networks prepared with a particular B_2 prepolymer and different imbalances as a function of the molecular weight of the B_2 prepolymer used in the reaction. The data are plotted in a similar way as the one used for the chain-extension reaction in Figure 4(a). The error bars account for a change of $\pm 5\%$ in the average value of r used to obtain the minimum fraction of soluble material.

The total concentration of the vinyl groups, located on the extremes of the B_2 prepolymer chains, which are available for the chain-extension or the crosslinking reaction, diminishes with the molecular weight of the chains. As the concentration of the vinyl diminishes, a higher stoichiometric imbalance is needed to obtain a reaction product with a maximum in M_w (in the linear case) or a minimum in W_s (in the crosslinking reaction). When the experimental results obtained from both systems are compared, the dependence of r is similar with the molecular weight of the prepolymer B_2 .

Figure 4(a,b) also reports the calculated values of the final extent of reaction reached in each of these systems. This has been done with the ex-

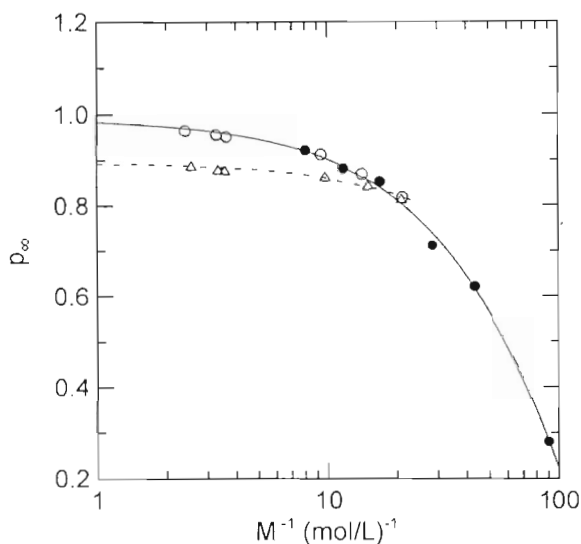


Figure 5. Final extent of reaction reached by hydrosilylation (p_{∞}) as a function of concentration of reactive groups in the initial mixture expressed as the inverse of molarity (M^{-1}). Symbols: (●) Chaumont et al.,¹⁸ (○) system $A_2 + B_2$, and (△) system $A_3 + B_2$; the solid and dashed curves represent the least-squares fit of the experimental data for the linear system and the network-formation system, respectively.

perimental data of the final molecular weight and the fraction of solubles from the linear and crosslinking reactions, respectively, and the well-known recursive approach proposed by Miller et al.²⁹ The effect of dilution of the initial reactive groups caused by the enlargement of the molecular mass of prepolymer B_2 is responsible for a decrease in the maximum extent of reaction in both cases.

In a previous work, we proposed (with[†] results available in the literature) an equation to quantify the influence of the initial concentration of reactive groups on the maximum extent of reaction of stoichiometrically balanced systems.²⁰ Figure 5 depicts the values of the maximum extent of reaction at the optimum stoichiometric imbalance (p_{∞}) as a function of the initial concentration of reactive groups (expressed as the inverse of molarity, M^{-1}) for the linear system ($A_2 + B_2$) and the network-formation system ($A_3 + B_2$). Values reported by Chaumont et al.¹⁸ for a linear system are also plotted.

Empirical equations obtained through a least-squares fit of the data are also drawn as solid and broken lines for the linear and network-forming systems, respectively. The equations corresponding to the lines are the following:

$$\begin{aligned} \text{system } (A_2 + B_2) p_{\infty} = & -1.2124 \\ & + 2.2057 \exp(-4.3031 \cdot 10^{-3} M^{-1}) \quad (1) \end{aligned}$$

$$\begin{aligned} \text{system } (A_3 + B_2) p_{\infty} = & -5.8712 \\ & + 6.7677 \exp(-5.5053 \cdot 10^{-4} M^{-1}) \quad (2) \end{aligned}$$

The maximum extent of reaction obtained in the linear system seems to be stabilized in a value of approximately 0.98, whereas in the networks the maximum extents of reaction obtained are near 0.89. The disagreement in p_{∞} between the data from the linear and crosslinked systems used in this work disappears when the concentration of reactive groups is lower than 0.066 mol/L, corresponding to a $M_{nB_2} > 30,000$ Da. A plausible explanation for the differences observed in the final extent of reaction between the linear and the crosslinking reactions may be the existence of impurities such as cyclic or linear low-molecular-weight nonreactive molecules in the commercial PDMS prepolymers used in this work. The extraction of the soluble fraction is much more sensitive to the presence of low-molecular-weight impurities than SEC that tends to be imprecise to detect low-molecular-weight fractions. Because of this, the final extent of reaction calculated from the weight fraction of soluble material in the $A_3 + B_2$ system should give lower values than those obtained from SEC measurements on the $A_2 + B_2$

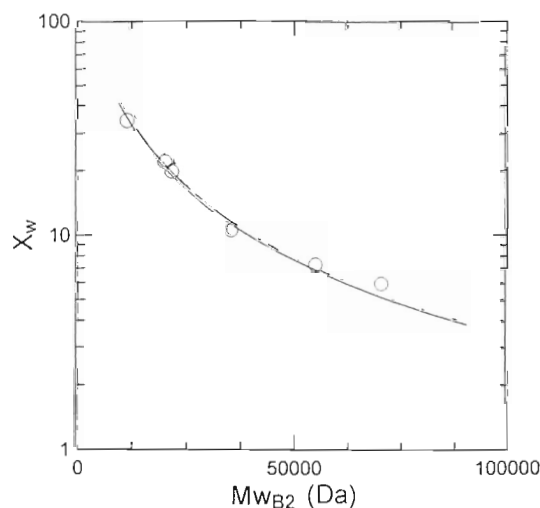


Figure 6. Maximum degree of polymerization on weight basis ($X_{w,max}$) for the system $A_2 + B_2$ as a function of the M_w of B_2 . Symbol: (○) experimental data. The solid line corresponds to the predictions of the recursive model considering eq 1.

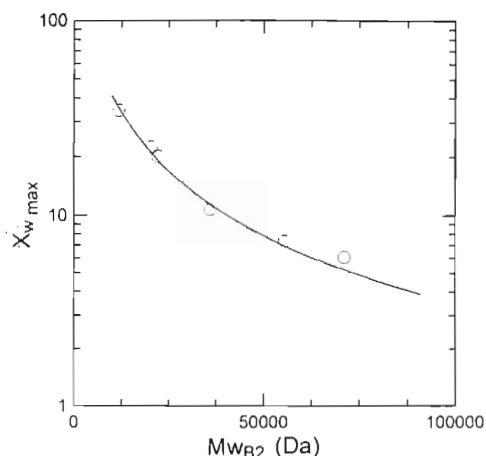


Figure 7. Minimum weight fraction of soluble material (W_{smin}) for the system $A_3 + B_2$ as a function of the M_w of B_2 . Symbol: (Δ) experimental data. The solid line corresponds to the predictions of the recursive model considering eq 2.

system. The differences between the two systems should be more important when prepolymers of low molecular weight are used. In this case, higher extents of reaction are obtained, implying lower fractions of solubility in the crosslinked systems. When the extracted fractions are low, the presence of small amounts of nonreactant impurities will induce greater errors in the estimation of the final extent of reaction for the $A_3 + B_2$ systems tending to give lower values for p_∞ .

Other possible causes for the observed discrepancies between the linear and the crosslinking reactions suggest that some diffusive control of the reaction may contribute to lower conversions in those networks that have a higher concentration of elastically active chains.

In the particular case of the linear system ($A_2 + B_2$), the maximum degree of polymerization

on weight basis (X_{wmax}) is a better parameter than the M_w that describes this effect. Figure 6 depicts values of X_{wmax} as a function of prepolymer molecular weight (M_{wB2}) obtained experimentally as compared with those calculated with the recursive method proposed by Macosko and coworkers,^{21,29,31} considering the effect of dilution given in eq 1. A decline in the degree of polymerization with increasing molecular weight of the prepolymer used in the polymerization is observed.

A similar analysis was conducted for the networks ($A_3 + B_2$) following the evolution of the minimum fraction of soluble material (W_{smin}), as shown in Figure 7. An increase in the amount of soluble material is observed when higher molecular weight prepolymers are used. Because the maximum extent of reaction decreases with the dilution of the terminal groups, networks with greater amounts of defects are obtained.

Observation of the results illustrated in Figures 6 and 7 in the range of molecular weights of B_2 analyzed, the hydrosilylation reaction does not behave as a completely ideal system. Even for the prepolymer with the lowest molecular weight studied, neither the degree of polymerization on weight basis (X_w) was sufficiently high nor the weight fraction of soluble material (W_s) was sufficiently low as predicted for an ideal maximum extent of reaction. Experimental and predicted values (eqs 1 and 2) of the maximum extent of reaction at M_{wmax} or W_{smin} have been presented, for both systems, in Table 2. Predicted values of X_w and W_s obtained with the recursive approach, considering the effect of dilution of reactive groups (eqs 1 and 2), agreed with experimental results for both systems in the range of molecular weights analyzed.

Table 2. Comparison of the Final Extent of Reaction Estimated from Experimental Measurements of Molecular Weight and Soluble Fractions on the ($A_2 + B_2$) and ($A_3 + B_2$) Systems with and the Values Given by eqs 1 and 2

| Polymer | System ($A_2 + B_2$) | | System ($A_3 + B_2$) | |
|---------|-------------------------|-------------------|-------------------------|-------------------|
| | p_∞ (Experiment) | p_∞ (Eq 1) | p_∞ (Experiment) | p_∞ (Eq 2) |
| D1 | 0.966 | 0.970 | 0.888 | 0.887 |
| D2 | 0.956 | 0.962 | 0.880 | 0.884 |
| D3 | 0.952 | 0.959 | 0.878 | 0.883 |
| D4 | 0.911 | 0.906 | 0.863 | 0.860 |
| D5 | 0.870 | 0.863 | 0.845 | 0.841 |
| D6 | 0.817 | 0.802 | 0.814 | 0.819 |

CONCLUSIONS

The reactions carried out with both systems revealed a difference in the value of the experimental stoichiometric imbalance (r_{exp}) for which a maximum in M_w (system $A_2 + B_2$) or a minimum in W_s (system $A_3 + B_2$) is obtained.

Empirical equations of maximum extent of reaction (p_w) as a function of initial concentration of reactive groups allows the prediction of molecular parameters obtained experimentally. However, eq 2 is only valid for concentrations higher than 0.019 mol/L because of the critical extent of reaction for this system (gel point).

Values of X_w for the system $A_2 + B_2$ as well as the W_s in the system $A_3 + B_2$ obtained experimentally confirms the influence of the initial concentration of reactive groups on the maximum extent of reaction reached in the hydrosilylation reaction catalyzed by the platinum salt *cis*-Pt[(C₂H₅)₂Si]₂Cl₂.

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