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Application of Polymer Network Theory to the Determination of Prepolymer Functionality

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ABSTRACT

Further work has been carried out on a new method of studying polymer network theory in an effort to find an accurate way of determining prepolymer functionalities. Model polyester systems containing tri-, di-, mono-, and nonfunctional molecules have been studied. In the majority of cases the results agree very well with the theory. In other examples the discrepancies can be explained by side reactions or unequal reactivity of similar functional groups. Some experiments were carried out with commerical prepolymer mixtures and these indicate that accurate results can also be obtained with these materials.

INTRODUCTION

In the formation of polymer network structures for critical applications, such as solid-propellant binders in rocket motors, it has been found that good processing and binding properties for

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these materials depend greatly on the functionality of the constituent prepolymer molecules [1]. In an effort to obtain these functionalities in isolation from considerations of molecular weight distribution in the prepolymers, a detailed study was carried out on polymer network formation criteria.

The major consideration was to see if methods could be found to overcome the problems of previous studies and obtain sufficiently accurate experimental verifications of the theory to give useful results in a practical determination of functionality.

As reported in detail elsewhere [2, 3], a new method of studying polymer gelation theory in polyesters was developed. Two key features of the system which had not been applied in combination in previous work were: first, the prepolymer reaction was driven to completion at the incipient gel point; and second, this gel point was determined by a viscosity change in the concentrated reaction mixture. These features enabled the problems of determining reaction extent in a partially gelled system to be avoided and gave a very accurate method of determining the incipient gel point.

The theoretical simplifications of the general polymer network theories, developed by Flory [4], Stockmayer [5], and others [6] to allow for complete reaction under nonstoichiometric conditions, have been reported in previous papers [3, 7, 8] and will not be developed here. This also applies to the experimental method and apparatus used [2].

The present paper is concerned with the extension of previous work to determine the experimental problems and limits of this method in more practical systems.

EXPERIMENTAL

The gel point determination procedure was the same as described previously [2] with the reagents mixed under nitrogen at 140°C by a high-speed stirrer-viscometer until the reaction was complete as determined by a leveling off in the viscosity. At the gel point there was a sharp increase in viscosity to very high values.

The materials used were purified by recrystallization until constant, sharp melting points were obtained and analysis (elemental and titration) results were within experimental error for the pure materials. p-Toluenesulfonic acid was used as the reaction catalyst.

DISCUSSION

In this study we continued to use highly-purified, saturated alcohols and acids in a polyesterification system as earlier work [9] had indicated that this avoided the side reactions which can occur in the previously studied polyurethanes [8] and alkyd resins [10]. The chain lengths of the model compounds used were chosen so as to minimize side reactions and possible cyclization reactions. Molecules with closely associated alcoholic groups susceptable to dehydration were avoided because they were shown to be particularly prone to decomposition in our acid catalyzed systems.

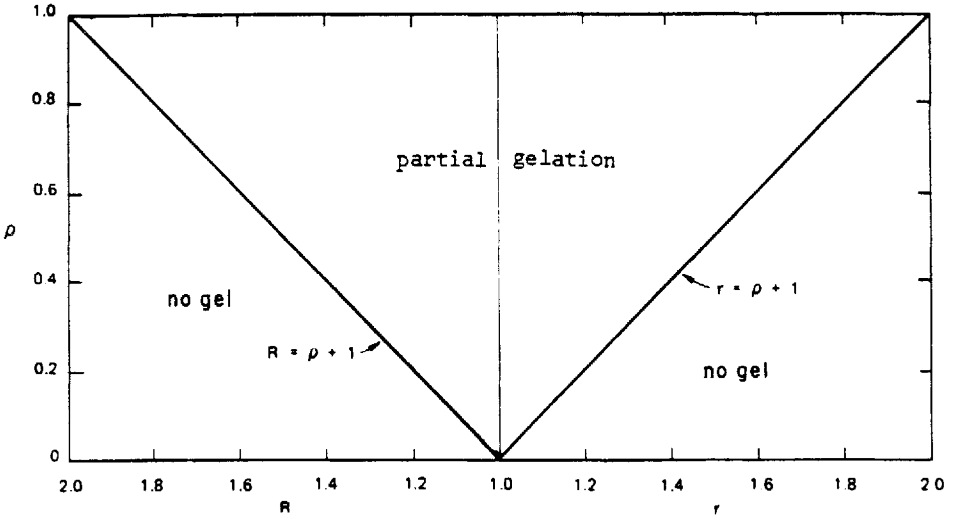

FIG. 1. Gelation plot for a simple (3,2/2) system at complete reaction where ρ = fraction of A groups contributed by the branch unit and R = 1/r = ratio of all A's to all B's.

Figure 1 shows a plot of the incipient gel equations for a system containing a trifunctional component and one difunctional component of a prepolymer containing Type A groups, and a difunctional component containing Type B groups (a 3,2/2 system), where the reaction is forced to completion for one type of component. The critical branching coefficient α is $\frac{1}{2}$ at the diagonal lines in the figure.

In the previously reported work decane diol and sebacic acid were used as the difunctional component and 1,3,5-pentanetricarboxylic acid (PTA) as the trifunctional material. As there were groups of different reactivity on the trifunctional component, modified equations, which led to plots and results [2] considerably different to those in

Fig. 1, had to be developed to account for this factor. To avoid the extra unknowns introduced by this differential reactivity, all work reported in the present paper was done under conditions of excess alcohol when PTA was the branching unit used.

As a first approach to materials which are more like the commercial prepolymers, we studied the effects of nonfunctional materials on the experimental determination of the incipient gel points. Network formation should not be effected by dilution with nonfunctional material unless cyclization reactions play a part in the reactions. The results (using the above model compounds) indicated that this was true over the range of diluent concentrations used (70 to 30%). Various hydrocarbon diluents were tried but the most convenient was found to be Nujol, mainly because of its ready availability in a pure form and its stability under the reaction conditions. In some reactions a phase separation occurred at the gel point and the sharp rise in viscosity at this point was occasionally followed by a sharp decrease due to the formation of small gel particles instead of a tightly bound gel mass. Extraction methods were usually carried out to confirm gel formation in these experiments.

Although the incipient gel points of the diluted, model-compound mixtures did not change significantly, the results showed that an optimum concentration of diluent could be found for the sharpest increase in viscosity at the gel point. The results in Table 1 were obtained at this dilution for the PTA, sebacic acid, decane diol system.

TABLE 1. Gel Point Results for a (3,2/2) System Containing Diluent (50% by Weight) Using PTA, $r > 1$

ρ_A[a]	α	±
0.100	0.492	0.005
0.198	0.500	0.003
0.297	0.500	0.003
0.396	0.500	0.003
0.495	0.500	0.003
0.588	0.500	0.003
0.685	0.500	0.003
0.784	0.500	0.003
0.891	0.500	0.003

[a] ρ_A = Fraction of acid groups contributed by the PTA.

In Table 1 the observed critical values of α in the second column were obtained using the experimentally determined quantities of reagents at the last point of complete reaction just before gelation and immediately after. These were artificially chosen in many of these experiments at point equidistant from $\alpha = 0.5$, the theoretical value. Thus the experimental incipient gel point at $\rho_A = 0.495$ is between $\alpha = 0.503$ and 0.497. The results were reproducible even when the gel point was approached by addition of different increments of triacid or even by the addition of diacid. This was the highest accuracy that could be obtained, even with purified materials under rigorous conditions. The amount of triacid needed to cause gelation in 20 g of reaction mixture close to gelation was often less than 10 mg, and mechanical problems of material addition made this the limit in gel point precision. These results were so close to the theoretically expected values that it is possible that slight impurities in the various reagents were balancing each other out. Less pure materials could be quickly detected by much larger errors in the incipient gel points.

The next step in an approach to commercial prepolymers was to substitute pure, high functionality prepolymers for model compounds. Emery Industry's Empol 1010 Dimer Acid, which is a carboxy-terminated prepolymer believed to be completely difunctional, with a molecular weight of 565 was used in a 3,2/2 system in the place of sebacic acid. The results are shown in Table 2. The values found under excess hydroxyl conditions were obtained using PTA as the cross-linking agent and decane diol as the alcohol in 50% Nujol (except where noted). The experimental α-values obtained are in excellent agreement with the proposal that the dimer acid is difunctional and the molecular weight is as stated. Results from experiments run under conditions of excess acid using trimethylol ethane (TME) and decane diol showed erratic and late gelation points. Earlier work [2] with TME as cross-linker with sebacic acid and decane diol in a 3,2/2 system had given very good results but this had been under conditions of excess hydroxyl groups.

Further experiments with these model compounds under excess acid conditions yielded the results shown in Table 3. The α-value reported here is the first point at which gelation occurred, due to the fact that in these experiments the point of gelation was erratic and much later than theoretically expected, and depended on such factors as the time of reaction and the method of approaching the gel point. It is believed that under conditions of excess acid the trimethylol ethane decomposes slowly and the darkening of the reaction mixtures would tend to support this view.

Erratic behavior was also noticed when attempts were made to determine the functionalities of hydroxyl- or carboxyl-terminated polybutadiene, polypropylene glycol, and other similar prepolymers under our reaction conditions. Thus, in order to study the effects of monofunctional components on network formation, we made model

TABLE 2. Gel Point Results for (3,2/2) Systems Containing Emery Diacid

Excess hydroxyl			Excess acid		
ρ_A	α	●	ρ_B	α	±
0.205	0.495	0.019	0.179	0.706	0.059
0.254	0.485	0.005	0.433	0.559	-
0.303	0.500	0.008	0.600	0.634	0.024
0.403	0.500	0.005			
0.510	0.500	0.005			
0.513[a]	0.500	0.005			
0.513	0.502	0.011			
0.514	0.504	0.028			
0.602	0.500	0.004			
0.702	0.501	0.004			
0.750[a]	0.513	0.002			
0.750	0.502	0.007			
0.801	0.501	0.003			
0.900	0.500	0.003			

[a] No solvent.

TABLE 3. Gel Point Results of TME Experiments (3,2/2) System, $R > 1$

ρ_B	α	$R_{(obs)}$	$R_{(calc)}$
0.119	0.578	1.087	1.119
0.211	0.534	1.184	1.211
0.228	0.576	1.168	1.228
0.264	0.561	1.207	1.264
0.515	0.560	1.405	1.515
0.621	0.542	1.526	1.621
0.750	0.517	1.700	1.750
0.766	0.543	1.645	1.766

prepolymers using either stearic acid or octadecanol as the monofunctional components. Because of the limitations placed on the choice of systems by differential reactivity and side reactions, the

TABLE 4. Gel Point Results for (3,2/2,1) System, PTA, $r > 1$[a]

ρ_A	f_A	f_B	α	±
0.254	1.902	2.0	0.501	0.003
0.505	1.905	2.0	0.498	0.002
0.751	1.905	2.0	0.501	0.001
0.254	2.0	1.901	0.496	0.005
0.505	2.0	1.905	0.498	0.002
0.752	2.0	1.905	0.504	0.001
0.251	1.801	2.0	0.499	0.002
0.504	1.802	2.0	0.500	0.002
0.752	1.800	2.0	0.504	0.001
0.255	2.0	1.802	0.505	0.003
0.504	2.0	1.802	0.499	0.002
0.753	2.0	1.802	0.503	0.001
0.254	1.705	2.0	0.500	0.003
0.506	1.701	2.0	0.504	0.002
0.752	1.702	2.0	0.505	0.001
0.27	2.0	1.7	No gel	-
0.507	2.0	1.698	0.503	0.002
0.755	2.0	1.702	0.510	0.001
0.504	1.50	2.0	0.504	0.002

[a] f_A and f_B are the functionalities of the carboxyl and hydroxyl model prepolymers, respectively.

cross-linker was again PTA, used under conditions of excess hydroxyl groups, and sebacic acid and decane diol were the difunctional components.

Table 4, which is an extension of previously published work [2], gives the results of these experiments. Again the results supported the theory. At the point where the functionality of the hydroxyl prepolymer was 1.7 and the ρ_A value was 0.27, no gel could be obtained, even when the experiment was repeated a number of times to values considerably past the expected gel point. However, this was very close to where theoretically no gel could form and only small amounts of impurity could place it in this category.

CONCLUSIONS

This work indicated that accurate functionality determinations in prepolymer systems could be accomplished by the use of gel point measurements. However, accuracy was greatly affected by side reactions and the differential reactivity of similar functional groups. In fact, none of the available, commercial, trifunctional materials and few of the prepolymers appear to be completely free from these faults under our reaction conditions. Thus further detailed study of more complicated model compound systems would be necessary before the method could be used for prepolymer functionality determinations.

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