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The application of size exclusion chromatography equipped with RI and LALLS detectors to study network formation

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Dedicated to Prof. Dragutin Fleš on the occasion of his 70th birthday

Abstract

The accuracy of the SEC/LALLS/RI method for measuring molecular weight and molecular weight distribution of the polymerizing system, consisting of a triisocyanate and a diol was examined. It has been found that both M_n and M_w were higher than theoretical up to about 60% conversion. Above this conversion M_w was considerably lower and molecular weight distribution narrower than predicted by gelation theory.

Introduction

It has been recognized for a long time that gelation in the polymerizing system occurs when the average functionality of the reacting components is greater than two. The first theory of gelation was proposed by Carothers who assumed that both number and weight average molecular weights go to infinity at the gel point[1]. Later Flory[2] and Stockmayer[3], using probabilistic approach developed a new gelation theory which could not only better predict the gel point but also allows calculation of the molecular weights and molecular weight distribution in the gelling system, as well as the several properties of the system before and after gel point. Recently, there has been revival of interest in the gelation phenomena since the structure of the networks is closely related to the mechanism of network formation. The knowledge of the structure is especially important for the further development of rubber elasticity theory. When endlinking of polyfunctional components is used to produce a crosslinked product, highly branched molecules are formed prior to gelation. It is of great practical and theoretical importance to know molecular weight, shape of macromolecules and molecular weight distribution during network formation. It is however difficult to test experimentally the existing theories due to limited precision of the experimental methods. The method of choice should provide information on the number (M_n) and weight average (M_w) molecular weights with high precision. With the advent of the low angle laser light scattering (LALLS) detector, the size exclusion chromatography (SEC) became the

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*To whom offprint requests should be sent most serious candidate as the method to study the course of the branching process before the gel point. Schosseler et al.[7] have applied successfully the SEC/LALLS method to study gelation of polystyrene in solution, crosslinked by gamma irradiation. However, they started from the high molecular weight precursor (approx. 55000). It is questionable if the same satisfactory precision of measuring molecular weights and molecular weight distribution can be obtained with low molecular weight starting compounds.

In this work we have examined the precision of the SEC coupled with refractive index (RI) and LALLS detector to measure simultaneously M_n and M_w of the model system based on relatively low molecular weight trifunctional and difunctional monomers. The results are compared with theoretical predictions and the precision of the experimental method assessed. Using SEC with RI/LALLS detectors it is possible to measure absolute molecular weights of the eluted polymer. In this work we have used tris (isocyanatophenil)thiophosphate (M=465), designated as DRF, and polypopyleneglycol (PPG) of molecular weight 1000. Number average molecular weight, $\overline{Mn}$, was calculated using the expression:

$$\overline{M}_n = \frac{\Sigma\ M_{Af}N_{Af} + \Sigma M_{Bg}N_{Bg}}{\Sigma\ N_{Af} + \Sigma N_{Bg} - p_A\Sigma f_{Ai}N_A} \qquad ....(1)$$

which in our case of equimolar ratio of NCO and OH groups is reduced to:

$$\overline{M}_n = \frac{2M_3 + 3M_2}{2 + 3 - 6p_A} = \frac{3930}{5 - 6p_A} \qquad ....(2)$$

Here, N_{Af} is the number of moles of the compound of functionality f, containing groups of the type A, and N_{Bg} is the number of moles of component containing groups B, having functionality g, M_{Af} and M_{Bg} are molecular weights of components of the type A and functionality f or type B and functionality g, while p_A is the conversion measured by disappearance of groups of the type A.

The theoretical weight average molecular weight was calculated from the expression derived by Macosco and Miller[4], which for the stoichiometric ratio of trifunctional (A) and difunctional (B) monomers is:

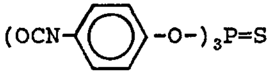
$$\overline{M}_w = \frac{(2/3)(1+p^2)M_A^2 + (1+2p^2)M_B^2 + 4pM_AM_B}{[(2/3)M_A + M_B](1 - 2p^2)} \qquad ....(3)$$

The advantage of the system used is due to the fact that both components can be obtained in very pure state, with well defined functionality, and slow reaction at room temperature, which allowed easy manipulation. The reaction was stopped at various conversions by blocking isocyanate groups with methanol. After the removal of methanol the sample was dissolved in tetrahydrofurane for analysis by SEC.

EXPERIMENTAL

Materials

Tris(4-isocyanatophenyl)thiophosphate was obtained from Bayer under trade name Desmodur RF, as 20% solution in methylenechloride. The purification was carried out by recrystallization from the concentrated solution at room temperature. Chemical formula of the isocyanate is:



Polypropylene glycol was purchased from Aldrich. Its molecular weight was 996 determined from the OH number. Water content was below 0.05%.

Methods

The synthesis was carried out at 23 °C in a three neck round bottom flask, supplied with stirrer, nitrogen inlet and outlet. Purified components were mixed at the stoichiometric ratio, heated to 90°C to melt the isocyanate and then cooled to room temperature. Samples of about 5 grams were taken at different times before gel point and titrated for the NCO content according ASTM D 1638-74. It was estimated that the precision of the conversion determination by NCO titration was about 1%.At the same time 5-10 grams of the sample were taken from the reaction flask and dissolved in methanol which reacted with the free NCO groups. Methanol was removed under high vacuum and the residue used for the size exclusion chromatography.

The molecular weights and molecular weight distribution was determined by means of size exclusion chromatography coupled to the CMX-100 Low Angle Laser Light Scattering Photometer (SEC/LALLS). The column set consisted of two Shodex A80M/S columns in series. The CMX-100, equipped with a stainless steel flow-thru cell, was used to monitor the on-line light scattering intensity (R_0) of the column eluent. An LDC/Milton Roy refractoMonitor III, refractive index detector, was used to provide the concentration data. The mobile phase consisted of stabilized THF. A flow rate of 1 ml/min was obtained by LDC/Milton Roy constaMetric IIIG pump. All data were processed via Real Time Data Acquisition with LDC/Milton Roy software, via an LDC/Milton Roy CMX-10A interface module (analog to digital converter) linked to a Digital Micro PDP-11/23 Plus computer. Sample solutions were filtered through a 0.45 um teflon membrane filter immediately before introduction to the CMX-100 sample cell. The specific refractive index increment, dn/dc, was determined via the KMX-16 Laser Differential Refractometer operating at 25°C in stabilized THF and at the same wavelength as that of CMX-100, i.e. 632.8 nm. The polymer optical constant, K, was calculated to be 5.9969×10^{-8} moles x cm^4/g^2, from the dn/dc value of 0.0863 ml/g and with a solvent refractive index of 1.4050 for the polyurethane samples. The dn/dc value did not significantly vary over a series of samples, therefore the mean dn/dc value was used for the calculation of K.

RESULTS AND DISCUSSION

SEC is a suitable method for the following of M_n and M_w simultaneously as well as for the direct assessment of the molecular weight distribution. Representative GPC curves obtained by RI and LALLS detectors for the sample no. 2, is given in Figure 1. Comparison of the calculated values of M_n and M_w with the experimentally determined values are given in Table 1. It should be mentioned that when UV/LALLS detector combination in conjunction with four Ultrastyragel column set was used, virtually the same results as those in table 1 were obtained, except that M_n values were somewhat higher.
The expressions (1), (2) and (3), used for calculation of molecular weights, are derived under assumption of equal reactivity of endgroups, which is in our case generally satisfied. Dusek et all.[5] have found slight positive substitution effect with DRF/PPG 1000 system, indicating that the second NCO group in the DRF will be more reactive after the first group reacted. This can cause widening of molecular weight distribution since it would favour increase of M_w above the values for the "ideal" case while M_n would be unaffected. Figurw 2. illustrates the change of theoretical and experimental molecular weights with conversion. The experimental M_n values were found to be systematically higher than the theoretical values, which is obviously caused by experimental error. On the other hand, experimental M_w were higher than theoretical values below about 60% conversion,

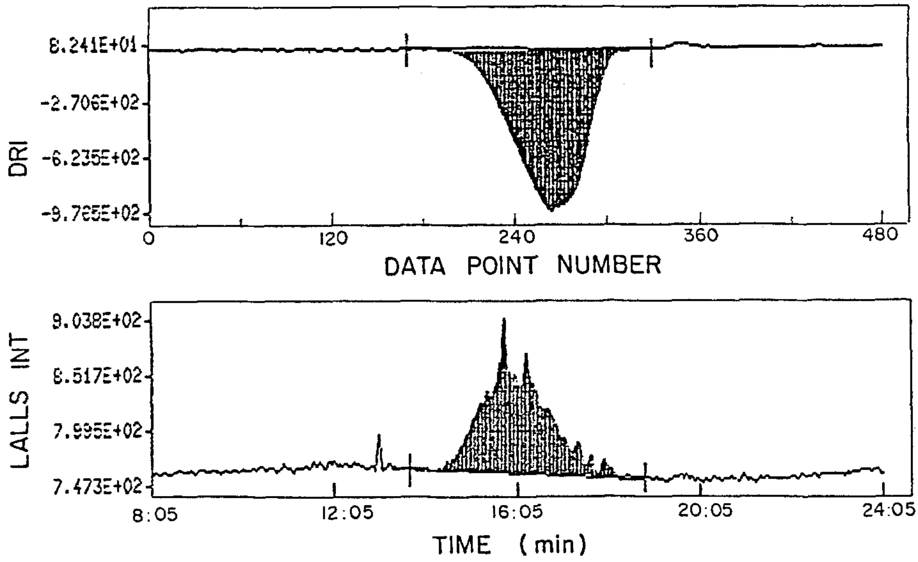


Figure 1. SEC curves of the sample at 56% conversion (no.2).

(corresponding to about $\bar{M}_w$=10000), while at higher conversions the reverse took place.

TABLE 1.
Calculated and experimental molecular weights at different degrees of conversion

	Sample No.				
	1	2	3	4	5
Conversion	0.384	0.564	0.624	0.684	0.70
M_n(theor)	1458	2432	3129	4386	4912
M_w(theor)	2354	6033	10833	40604	133465
M_w/M_n(theor)	1.61	2.48	3.46	9.58	27.2
M_n(exp)	2300	2700	3800	5000	3900
M_w(exp)	4200	6200	10000	16800	23400
M_w/M_n(exp)	1.83	2.30	2.63	3.36	6.83

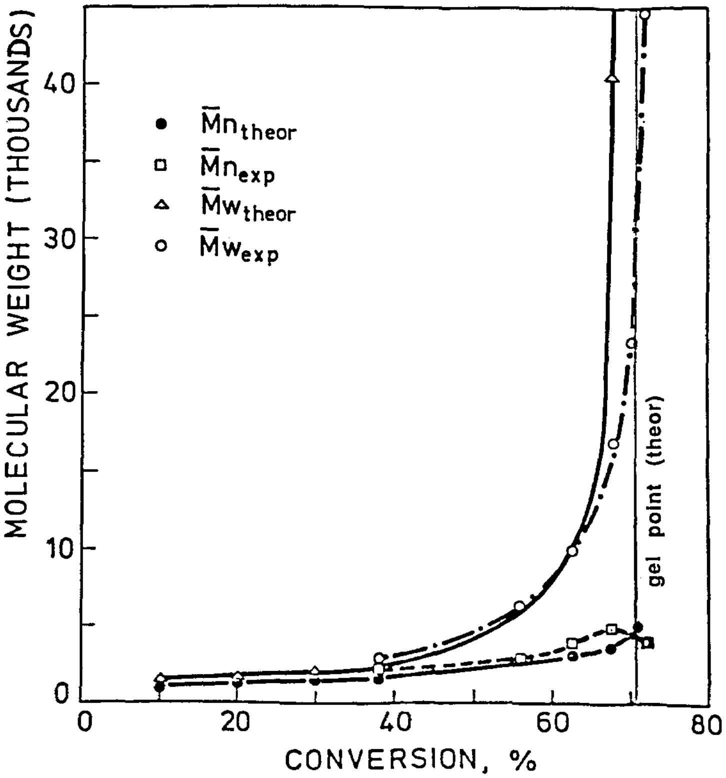


Figure 2. Comparison between theoretical and experimental molecular weights at different conversions.

In the case of existence of intramolecular reactions, experimental values of both M_n and M_w are expected to be lower than the corresponding theoretical values. Figure 3 illustrates the difference between theoretical and experimental values (M_n(theor) - M_n(exp) and M_w(theor) - M_w(exp)) vs. conversion. Figure 3. shows that at 40% conversion both M_n and M_w theoretical values are lower (negative difference) by 50%, but the difference become small at about 60% conversion to be very positive with M_w near the gel point. As stated before, only the positive difference is expected due to possible intramolecular reactions which were really found by following M_n change with conversion using vapour pressure osmometry (VPO).[6]

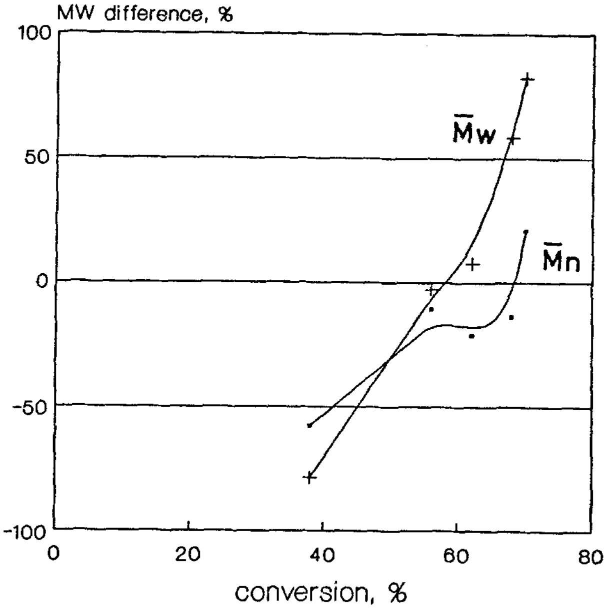


Figure 3. The difference between theoretical and experimental values of molecular weights at different conversions.

In the case of ideal reaction (without intramolecular reactions and at equal reactivity of the reacting groups) the gel point should occur at 70.7% conversion and M_n at the gel point for this system should be 5189, while M_w goes to infinity. It has been found however, that M_n values obtained by VPO for this system are generally lower than theoretical and the gel point is about 1% higher than in the ideal case[6]. This work showed that although SEC/LALLS/RI method is suitable for measurement of the molecular weight distribution of the branched polymers, and in spite of the relatively sophisticated equipment used, it is not precise enough to test gelation theories. It has been found that the error depends on the molecular weight. The problem is probably related to the low precision of the light scattering method at low molecular weights (below 5000). However, even at high conversions the measured weight average molecular weights appeared to be much lower than predicted by gelation theory, giving thus much narrower molecular weight distribution compared to the theoretical predictions, which could not be explained by the occurrence of intramolecular reactions. For example, M_w at p=0.70 was 23400 which in ideal polymerization should be obtained at p=0.6675, implying that 3.25% of the total NCO groups were waisted in various side reactions, which contradicts previous findings, even if an error of 1% in measuring conversion is taken into account.

CONCLUSIONS

- The use of SEC in conjunction with RI and LALLS detectors, did not show satisfactory precision required to test the predictions of gelation theories, when relatively low molecular weight monomers were used. The error was dependent on molecular weight. The values of M_n and M_w from SEC/LALLS measurements were higher than predicted up to molecular weight of about 5000, which was ascribed to the insufficient precision of the LALLS method at low molecular weights.
- The molecular weight distribution was much narrower than predicted by theory, particularly at high conversions, which can not be accounted for by intramolecular reactions.

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