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Effective Functionality of Isocyanate- and Thiol-Terminated Polymers

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ABSTRACT

A simple method to give an approximate value for the effective functionality of isocyanate- and thiol-terminated polymers has been developed. A solution of the polyisocyanate is titrated into a polyamine, or iodine into a polythiol, until a gel forms. The titer gives the extent of reaction at the gel point, hence the functionality. Intramolecular reactions occur giving a low apparent functionality, and it is necessary to extrapolate to infinite concentration. The volume and the extent of intramolecular reactions is changing during a titration; thus there is some uncertainty in the functionalities obtained. This and other limitations of the method are discussed. The method has been used with some polyisocyanates based on poly(propylene oxide) polyols and with some commercial thiol-terminated polymers. The oxidation of polythiols and the reaction of polyisocyanates with water can be considered examples of the self-condensation of RA_f monomers. The extent of reaction of the gelation of a polyisocyanate with water has been determined and found to agree with Flory's theoretical prediction.

INTRODUCTION

Polyfunctional isocyanate- and thiol-terminated polymers are used in shrink-resist and durable-press finishes for wool [1, 2], although they find more extensive use in other industrial applications such as coatings and elastomers [3]. Control of the structure formed on curing of these polymers is important, and hence simple methods to determine their functionality are desirable.

The functionality of polymers can be obtained from molecular weight determinations, but a more useful approach is gel point experiments [4-6]. Fogiel [4] has described a method to determine the effective functionality of a polyisocyanate in which it is reacted with various amounts of a diol with hydroxyl groups of equal reactivity. Some mixtures gel whereas others do not, a point where there is just sufficient polyisocyanate to gel excess diol may be found. At this point all isocyanate groups have reacted and the extent of reaction of the hydroxyl groups (p) is given by the proportion of reactants used initially. The weighted-average functionality is then obtained from Eq. (1), which is derived from Stockmayer's [7] equation for gelation.

$$p = (f - 1)^{-1} \qquad (1)$$

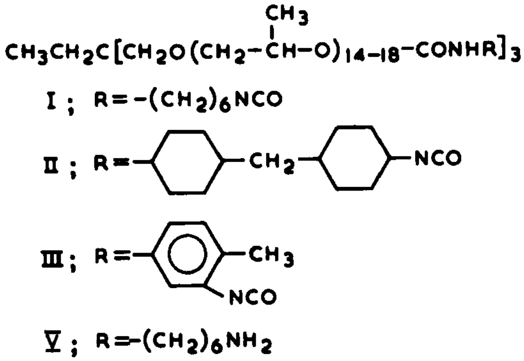
The value of Fogiel's [4] method is that it is applicable to the case of unequal reactivity isocyanate groups, since it uses a point where they are completely consumed. The other methods [5, 6] of functionality determination require that the isocyanate groups have equal reactivity which is not the case, for example, with polyisocyanates derived from tolylene diisocyanate [3].

Fogiel's method [4] requires a number of separate experiments, but if the gelation reaction is fast it should be possible to obtain p from a single experiment simply by slowly titrating in one reactant into the other until a gel just forms. It would be necessary for the reactants to be mixed faster than they react and their reaction product to be soluble, so that the whole solution forms a distinct gel. We examine here this possibility with some isocyanate- and thiol-terminated polymers.

DISCUSSION

Effective Functionality of Polyisocyanates

The reaction of isocyanates and amines is very fast [3]; polyisocyanate I and one equivalent of ethylenediamine gel in 10 sec in dioxane at 20° C. When solutions of polyisocyanates I-III were titrated into well stirred solutions of various diamines, no localized gel formation was observed, and eventually a point was reached at



$CH_3CH_2C[CH_2O(CH_2-\overset{CH_3}{\overset{|}{C}}H-O)_{14-18}-CONHR]_3$

I; $R=-(CH_2)_6NCO$

II; R=

III; R=

V; $R=-(CH_2)_6NH_2$

which the whole solution gelled. This indicates that, even though reaction is fast, it was possible to mix the solutions faster than they could react. In these titrations a sharp distinct gel point was obtained, and the titers to the gel point were found reproducible, provided the rate of addition of the polyisocyanate solution was slow and the solution not too concentrated. In concentrated solutions even mixing was not possible, and gel began to separate before the endpoint. This resulted in the addition of excess polyisocyanate to gel the reaction mixture completely. The concentrations of the titrating solutions were chosen to avoid high concentrations. Some typical results are shown in Table 1. The gel point was markedly concentration-dependent due to intramolecular reactions.

Correction of Apparent Functionalities for Intramolecular Reactions

Intramolecular reactions in polydisperse polyfunctional condensations have been considered theoretically by Kilb [8], but it could be questioned whether this treatment is valid for the type of molecular weight distributions likely to be found in polyisocyanates I-IV. In studies of the gelation of polyisocyanates and diols [4], and poly(propylene oxide) triols with hexamethylene diisocyanate [9], linear relationships were found between the reciprocal concentration and apparent functionality, in agreement with Kilb's [8] predictions.

TABLE 1. Titration of Polyisocyanate I into 1,6-Diaminohexane

Titer of 0.18 N polyisocyanate in dioxane to the gel point (ml)	Volume of dioxane solution containing 0.283 g of 1,6-diaminohexane (ml)	Apparent functionality
13.75	50	2.96
15.50	75	2.74
17.25	100	2.57
18.75	125	2.44
20.25	150	2.33
21.75	175	2.24
No gel	225	<2
No gel	275	<2

These studies calculated concentrations in slightly different fashions; Fogiel [4] used the initial molar concentration of one of the reactants (the hydroxyl groups) whereas Hopkins et al. [9] used the sum of initial molar hydroxyl and isocyanate concentrations. Kilb's [8] treatment considers the volume of polymer present which would appear to be better approximated by the method of Hopkins et al. [9], although it might be expected both methods would extrapolate to the same point.

Hopkins et al. [9] found some deviation from the linear functionality-reciprocal concentration relationship at high concentrations, whereas Fogiel [4] did not. Hopkins et al. [9] assumed that the poly(propylene oxide) triols used had a functionality of exactly three, although several studies [4, 10, 11] of poly(propylene oxide) triols have found that these have a lower functionality. If the data of Hopkins et al. [9] are reinterpreted along these lines there is less deviation from linear relationships at high concentrations.

These findings suggest that in the present gelations of polyisocyanates with diamines, extrapolation of a plot of the reciprocal concentration against apparent functionality to infinite concentration should give a value close to the true effective weighted-average functionality. However, in our titration experiments the volume and thus the extent of intramolecular reactions are changing during titration. The titrant has been chosen to keep the volume increase small, but the relative

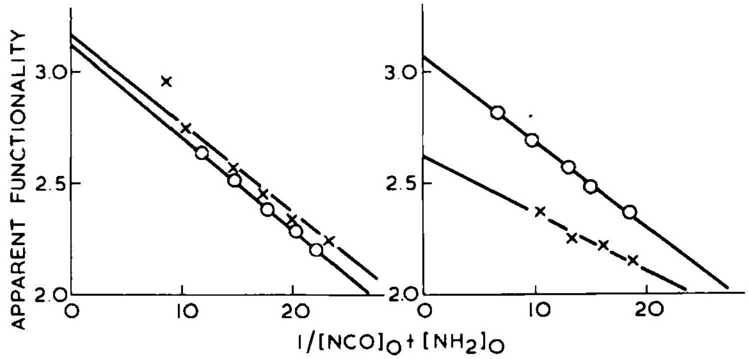


FIG. 1. Effect of concentration on apparent functionality of polyisocyanates: (left) titration of polyisocyanate I into (×) 1,6-diaminohexane and (o) 1,12-diaminododecane; (right) (×) titration of polyisocyanate III into 1,6-diaminohexane and (o) titration of polyisocyanate II into 1,6-diaminohexane.

volume change will be greater in concentrated solutions giving a larger error. To calculate concentrations we have arbitrarily chosen the volume at the gel point. Figure 1 shows some plots of apparent functionality against the reciprocal of the sum of the initial molar concentrations of amino and isocyanate groups in the volume at the gel point. Good linear relationships were obtained. Further results are summarized in Table 2. When Fogiel's [4] method of calculation of concentration i.e., the initial molar concentration of amino groups, was used, an extrapolated effective functionality obtained was 0.1 lower in each case.

The effective functionality obtained for polyisocyanate I by titration with hexamethylenediamine, is in good agreement with a value of 3.2 ± 0.1 obtained by Jackson and Solomon [5] for a very similar polyisocyanate in a conventional gelpoint experiment with 1,4-butanediol.

Errors in Functionality Titrations

There are several sources of error in this titration method for determining polyisocyanate functionality. The volume change during a titration gives a high extrapolated functionality. If the concentrations

TABLE 2. Effective Functionalities from Polyamine–Polyisocyanate Titrations

Titrant	Reactant	Effective functionality (extrapolated to infinite concentration)
Polyisocyanate I	1,2-Diaminoethane	3.0
Polyisocyanate I	1,3-Diaminopropane	2.9
Polyisocyanate I	1,6-Diaminohexane	3.2
Polyisocyanate I	1,12-Diaminododecane	3.1
Polyisocyanate I	Jeffamine ED-900[a]	3.1
Polyisocyanate II	1,6-Diaminohexane	3.1
Polyisocyanate III	1,6-Diaminohexane	2.6
1,6-Diaminohexane	Polyisocyanate I	3.6
1,6-Diisocyanatohexane	Polyamine V	3.8
Polyisocyanate I	Polyamine V	3.6[b]
Polyisocyanate IV	Polyamine V	2.2[c] 2.1[d]

[a] Amino-terminated ethylene oxide-propylene oxide copolymer (Jefferson Chemical Co.), molecular weight 900, assumed to be difunctional.

[b] Functionality 3.2 assumed for polyisocyanate I.

[c] Functionality 3.6 assumed for polyamine V.

[d] Functionality 3.8 assumed for polyamine V.

are calculated at a volume halfway through the titration, the effective functionalities are reduced by 0.1. Separation of gel before the endpoint gives a low apparent functionality. As both these errors are most pronounced in concentrated solutions, in the extrapolation the point at highest concentration was disregarded.

The apparent functionality tends to be low if the amino groups of the diamine do not have equal reactivity. This appears to be a reasonable assumption with 1,6-diaminohexane, but the results in Table 2 suggest that the amino groups of ethylenediamine and 1,3-diaminopropane do not have exactly equal reactivity. In addition, unless the isocyanate groups have exactly equal reactivity, the diamine must be in excess (i.e., it is the reactant not titrant). When the titration was performed in the reverse direction, i.e., titrating 1,6-diaminohexane into polyisocyanate 1, a higher functionality was obtained (Table 2) indicating that isocyanate groups of I did not have exactly equal reactivity.

Limitations of the Polyisocyanate Functionality Titration Method

The method could not be used for all polyisocyanates, as it is necessary to have a solvent in which the polyurea produced during the reaction is soluble. Suitable solvents could not be found for the gelation of 1,6-diaminohexane with the polyisocyanates Desmodur N (Bayer), a biuret triisocyanate derived from the reaction of hexamethylene diisocyanate and water, or Imprafix TH (Bayer), the product from reaction of trimethylol propane with tolylene diisocyanate, or the isocyanurate trimer from 2,4-tolylene diisocyanate. With these polyisocyanates precipitation occurred before the gel point.

The method was also unsatisfactory when the functionality was close to two, as only concentrated solutions would gel. Intramolecular reactions prevented gelation in more dilute solutions. To overcome this problem, diethylene triamine was examined as a reactant but as expected was unsatisfactory due to the unequal reactivity of the amino groups. In an attempt to obtain a polyamine with amino groups of equal reactivity, polyisocyanate I was hydrolyzed with hydrochloric acid to polyamine V. Gelation titrations with polyamine V (Table 2), suggest that there may have been some increase in functionality during the preparation of V (presumably by urea formation), and the amino groups may not have exactly equal reactivity.

The main use of polyamine V would appear to be for comparing a series of similar polyisocyanates. Comparing functionalities obtained by using polyamine V with those obtained by using diamines may not be valid. Polyamine V could be satisfactorily titrated against polyisocyanate IV, which could not be satisfactorily titrated against 1,6-diaminohexane.

Utility of Polyisocyanate-Diamine Functionality Titrations

In spite of the uncertainty introduced by intramolecular reactions, the titration method is simpler and quicker than previous methods

[4-6] for determining polyisocyanate functionality; for example, Fogiel [4] indicates with his method that a month should be left to determine whether gelation has occurred.

As the isocyanate-amine reaction is much faster than isocyanate hydrolysis, it was not necessary rigorously to exclude moisture from the system as in previous methods [4-6] to determine isocyanate functionality. We found that propan-2-ol could even be used as solvent for the gelation of polyisocyanate I and diamines; the effective functionalities obtained were only slightly lower than when dry dioxane was used.

The main value of these polyisocyanate functionality determinations is in comparing a series of related polyisocyanates, for example I-IV, which have all been found [12] to produce shrink resistance in wool, where direct molecular weight determinations may not show significant differences. The functionality differences in this series reflect different extents of thermal side reactions [3] during preparation (e.g., isocyanate polymerization or allophanate and biuret formation), or capping and chain extension reactions (where one or both isocyanate groups of a diisocyanate react).

With dissimilar materials the method is mainly of use to predict the extent of reaction in other gelation reactions rather than to obtain molecular weight data. For example, the functionalities obtained by gelling a series of polyisocyanates with a common polyamine could be used to compare the degree of crosslinking when each is cured by some means.

Functionality determinations have limited uses in the structural determination of unknown polyisocyanates, as reaction with water or thermal reactions of isocyanates can change the functionality considerably. In these cases, to determine the nature of the parent polyol, it would be necessary to hydrolyze and isolate the polyol, for example, by using Jackson and Solomon's method [5].

Thiol-Terminated Polymers

When thiol-terminated polymers are used to shrink-resist wool they are crosslinked by aerial oxidation to polydisulfides [2], but in other applications other crosslinking reactions may be used [13]. The oxidation of polythiols, particularly with iodine, can be considered as an example of the self-condensation of an f-functional monomer, RA_f, which was discussed by Flory [14]. The extent of reaction at the gel point p_c for such self-condensations is given [15] by Eq. (2). For this to be valid there must be no build-up of intermediate oxidation products which could occur, for example, if the

$$p_c = (f - 1)^{-1} \tag{2}$$

reaction actually forming the disulfide bonds was rate-limiting, or if further oxidation occurred to noncrosslinked products such as sulfonic acids.

Equation (2) for polythiol oxidation can be derived from Stockmayer's equation [7] by using Fogiel's [4] arguments in a similar fashion to Eq. (1) by assigning the oxidant a functionality of two, since it joins together two thiol groups on reaction, and considering only the concentration of oxidant actually consumed.

The reaction of thiol-terminated polymers with iodine was found to be sufficiently rapid for a titration method to determine functionality. In most solvents, addition of iodine to polythiols gave an immediate precipitate which entrained some iodine and slowly reacted further with iodine. Satisfactory results could only be obtained with dimethylformamide as solvent and on titrating with 0.1 N iodine in water containing potassium iodide. The reaction of polythiols with iodine appeared to be slower in dimethylformamide than in other solvents. In these titrations, there was no clear gel endpoint, and gelatinous material began to separate a little before the iodine color endpoint, which was quite reproducible.

Table 3 shows some results with some thiol-terminated poly(propylene oxides) (Oligan series, Ciba-Geigy) which are used to shrink-resist wool [2], and also thiol-terminated polysulfides (LP series, Thiokol Corp.). The method was used directly on one product (Oligan

TABLE 3. Effective Functionality of Commercial Polythiols

Product	Manufacturer	Backbone	Effective functionality
Resin EP262[a]	Ciba-Geigy	Poly(propylene oxide)	2.4
Oligan 500	"	"	2.8
Oligan SW	"	"	2.8
LP-3	Thiokol	Polysulfide	< 2.1
LP-8	"	"	2.4
LP-31	"	"	2.5
LP-33	"	"	2.5

[a] No longer manufactured.

SW, Ciba-Geigy) in the form of a 50% emulsion, without isolating the polythiol. The functionalities were calculated by assuming that there was a linear relationship between the apparent functionality and the reciprocal of the concentration of thiol groups originally present in the volume present at the iodine endpoint.

There are a number of sources of error in this method of polythiol functionality determination, so that the method has very limited usefulness. The volume change during a titration gives a high apparent functionality, whereas gel precipitation before the endpoint and the possibility of oxidation beyond the disulfide stage gives a low apparent functionality. Furthermore, during the titration, the polythiol is in excess, so the method is valid only for the case in which the thiol groups have equal reactivities. In addition, the method cannot be used for functionalities below two and is not satisfactory for functionalities close to two.

Titration methods could obviously be used to determine the functionalities of other types of polymer, provided a sufficiently fast polycondensation reaction could be found.

Self-Condensation of RA_f Monomers

There has been some discussion in the literature on the validity of Eq. (2) for the self-condensation of RA_f monomers. Masson and co-workers [16-18] have proposed an alternate treatment to Flory's [13] which gives an extent of reaction at the gel point of 2/f. This has been discounted by several authors [19-22], but no condensations of this type appear to have been studied experimentally. The earlier treatment of Carothers [23] also predicts a value of 2/f for the RA_f condensation.

As well as the oxidation of polythiols, the reaction of a polyisocyanate with water also appears to be an example of an RA_f self-polycondensation. The reaction of isocyanates with water is known [3] to involve a slow rate-determining hydrolysis [reaction (3)] followed by rapid urea formation [reaction (4)]. Thus, the initial water concentration will influence the rate of gelation, but only marginally the extent of reaction at the gel point, provided reaction (4) is very much faster than reaction (3).

$$\mathrm{RNCO} + \mathrm{H_2O} \xrightarrow{\text{slow}} \mathrm{RNH_2} \qquad (3)$$

$$\mathrm{RNH_2} + \mathrm{RNCO} \xrightarrow{\text{fast}} \mathrm{RNHCONHR} \qquad (4)$$

We have examined the gelation of polyisocyanate I with water in dioxane (see experimental section) and found the extent of reaction at the gel point to be 0.53. For a value of 3.1 (obtained from Fig. 1) for polyisocyanate I at the concentration used in this gelation, the extent of reaction calculated according to Eq. (2) is 0.49. This appears to confirm Flory's [14] treatment of the RA_f self-condensation.

EXPERIMENTAL

Preparation of Polyisocyanates

The dried polyol and 10% molar excess of diisocyanate were heated under nitrogen in the absence of solvents or catalysts for the times and temperatures shown in Table 4. The isocyanate content [3] was determined by adding excess 0.1 N di-n-butylamine in propan-2-ol and back-titrating with 0.1 N hydrochloric acid to a Bromophenol Blue endpoint.

Effective Functionality of Polyisocyanates

A 0.2 N solution of the polyisocyanate in dry dioxane and a 0.1 N solution of 1,6-diaminohexane (or other polyamine) in dry dioxane were prepared and standardized against 0.1 N hydrochloric acid. Laboratory-reagent 1,6-diaminohexane was used and found to be more than 98% pure by titration with acid.

The amine solution (50 ml) was pipetted into a beaker containing a magnetic stirring bar and stirred as rapidly as possible while slowly titrating in the polyisocyanate solution. About half the required amount of polyisocyanate was added in one portion, then the remainder added in 1-ml portions, with about 20-sec intervals between additions. Near the endpoint, smaller additions were made. The gel point was quite sharp and was reproducible to about 0.25 ml. At the gel point the vortex disappeared and the stirrer bar slowed down or stopped. The titration was repeated, diluting the amine solution with 25, 50, 75 ml etc., of dry dioxane.

The extent of reaction is given by t/t_0 where t is the titer and t_0 the titer expected for 100% reaction. The apparent functionality was calculated according to Eq. (1) and plotted against the reciprocal of the sum of the initial molar concentration of isocyanate and amine groups required for gelation in the volume present at the gel point. The effective functionality was obtained by extrapolation of the least-squares plot to infinite concentration (i.e., $1/[NCO]_0 + [NH_2]_0$

TABLE 4. Preparation of Polyisocyanate Prepolymers

No.	Structure	Polyol molecular weight	Source	Diisocyanate	Temp (C)	Time (hr)	Isocyanate content
I	Poly(propylene oxide) triol	3000	Desmophen 3400 (Bayer)	Hexamethylene diisocyanate	100	8	3.5
II	"	3000	"	Hylene W (du Pont)[a]	110	1	3.0
III	"	3000	"	2,4-Tolylene diisocyanate	60	8	3.9
IV	Poly(propylene oxide) diol	2000	Voranol P2000 (Dow)	Hexamethylene diisocyanate	100	8	3.5

[a] Bis(4-isocyanatocyclohexyl)methane.

becomes zero). The point at highest concentration was disregarded, since the apparent functionality is likely to be in error.

Polyamine V

Polyisocyanate I (400 g) was dissolved in dioxane (500 ml) and concentrated hydrochloric acid (100 ml) added. After 24 hr the mixture was evaporated in vacuo on a rotary evaporator. The residue was dissolved in water (1 liter), excess concentrated ammonia added, and polyamine V (350 g) extracted with methylene chloride.

Effective Functionality of Polythiols

Iodine in water (0.1 N) containing potassium iodide was prepared by using BDH concentrated volumetric ampoules. The thiol content of the polythiol was determined by titrating polythiol solutions in propan-2-ol or propanol-dimethylformamide mixed solvent against iodine solution. The presence of a large volume of propan-2-ol appears to favor intramolecular reactions and prevent gelation.

For the functionality determination the 0.1 N iodine was titrated into magnetically stirred 25-ml aliquots of a 0.1 N solution of the polythiol in dimethylformamide to which various amounts of extra amounts of dimethylformamide had been added. The color change of the iodine endpoint was quite sharp and reproducible, but gel began to separate some time before, often as a large blob attached to the stirring bar.

The titer to the iodine endpoint gave the extent of reaction at the gel point, and this was used to calculate the apparent functionality by Eq. (2). The reciprocal of the initial molar concentration of thiol groups in the total volume at the iodine endpoint was calculated and plotted against the apparent functionality. Extrapolation to infinite concentration (i.e., zero reciprocal concentration) gave the effective functionality.

Gelation of Polyisocyanate I with Water

A 0.125 N solution of polyisocyanate I in dioxane containing 0.56 M water was allowed to stand at 20 C. Aliquots were removed and the isocyanate content was determined as above. After a day the reaction became first-order with respect to isocyanate, and the solution gelled after 19 days. The isocyanate content at the gel point was obtained by extrapolation from a first-order rate plot.

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