Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Functionality and Functionality Distribution Measurements of Binder Prepolymers

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To cite this Article Muenker, Adolf H. and Hudson Jr., Boyd E.(1969) 'Functionality and Functionality Distribution Measurements of Binder Prepolymers', Journal of Macromolecular Science, Part A, 3: 7, 1465 — 1483
To link to this Article: DOI: 10.1080/10601326908051837
URL: http://dx.doi.org/10.1080/10601326908051837

J. MACROMOL. SCI.–CHEM., A3(7), pp. 1465-1483, November, 1969

Functionality and Functionality Distribution Measurements of Binder Prepolymers

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SUMMARY

The functionality of a prepolymer, which is defined as the ratio of molecular weight to equivalent weight, is probably the most important single parameter that determines the properties of the cross-linked polymer network. The determination of prepolymer functionality therefore requires accurate knowledge of both number average molecular weight and equivalent weight. Ideally, a suitable prepolymer for propellant binder applications has terminal functionality (OH or COOH). Such a prepolymer theoretically has a functionality of 2.0. Because of uncontrolled chain termination reactions during the prepolymer synthesis, however, not all polymer chains have the desired functional end group. As a result, prepolymers generally have a distribution of functionalities, including nonfunctional, monofunctional, and the desired difunctional prepolymer.

Number average molecular weight measurements have been carried out by vapor pressure osmometry (VPO). All molecular weight measurements were extrapolated to infinite dilution, $(\bar{M}_n)_0$, to eliminate effects due to 1) polymer-polymer association and 2) polymer-solvent interaction.

Equivalent weight determinations of both COOH- and OH-functional prepolymers were based on infrared absorption measurements of polymer solutions. In the case of OH-functional prepolymers, a second, independent method was developed which is based on the reaction of the prepolymer with p-toluenesulfonyl isocyanate, a very reactive isocyanate. Both methods can accurately determine the equivalent weight of 50- to 100-mg polymer fractions.

The method we have developed to determine the functionality distribution of binder prepolymers is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono-, and difunctional components. Prepolymers which have been characterized by this technique include OH-terminated hydrogenated polybutadienes, COOH-terminated hydrogenated polybutadienes, and COOH-terminated polyisobutylenes. Typical prepolymer samples analyzed to date contain 0-7% nonfunctional polymer and 16-33% monofunctional polymer.

INTRODUCTION

The problem of making high-quality binders with reproducible physical properties depends upon the synthesis of functionally terminated prepolymers with reproducible molecular weight and functionality as well as the distribution of these qualities. Mechanical properties of the cured propellant are affected by the molecular weight and functionality distribution of the prepolymer.

In order to obtain reproducible prepolymers, it is essential that analytical methods be available to measure these prepolymer characteristics. A number of methods are available for the determination of molecular weight distribution of prepolymers, notably fractional precipitation or solution and, more recently, gel permeation chromatography. No method was known, however, which could determine the functionality distribution of prepolymers, although this prepolymer quality parameter has a more serious effect on propellant mechanical properties than does molecular weight distribution. Monofunctional prepolymer components will seriously affect the mechanical properties of the propellant since monofunctional polymer chains will act as chain terminators during the cure process and hence interfere with the formation of a large polymer network needed to impart good mechanical properties to the propellant. Nonfunctional prepolymer components act as high-molecular-weight plasticizers and cannot participate in the cure process. The overall functionality of a prepolymer as determined from molecular weight and equivalent weight determinations does not permit a quantitative estimate of the percentages of non-, mono-, and difunctional components present in the polymer.

Manufacturers of binder prepolymers have generally assumed that low functionality is primarily due to the presence of nonfunctional prepolymer components. Our functionality distribution measurements have shown that the bulk of low functional polymer components is monofunctional rather than nonfunctional.

DISCUSSION AND RESULTS

Molecular Weight Measurements

The accuracy with which the functionality of a given prepolymer can be measured depends on the accuracy with which number average molecular weight and equivalent weight can be measured. From an examination of available test methods and their limitations for number average molecular weight measurements, we selected vapor pressure osmometry (VPO) as the most suitable method for the low-molecular-weight range (1000-5000) of interest in connection with binder prepolymers [1]. Vapor pressure osmometry (VPO) is a thermoelectric differential vapor pressure technique for determining number average molecular weight ($\bar{M}_n$) of polymers of low or moderate molecular weight. The thermoelectric method has significant advantages in speed and in small sample size. The basis of the thermoelectric method is the measurement of the small temperature difference resulting from a differential mass transfer between droplets of pure solvent and polymer solution maintained in an atmosphere of solvent vapor.

Low functionalities of binders have traditionally been blamed on errors in the number average molecular weight measurement. It is true that molecular weight measurements can be seriously lowered by the presence of low-molecular-weight impurities, notably residual solvent and antioxidants. If possible, molecular weight measurements should therefore be carried out after all residual solvent has been removed and before antioxidant is added to the prepolymer. There are other factors, though, which must be considered: (1) There is the possibility of polymer-polymer association which leads to an apparently higher molecular weight, and (2) there is the general phenomenon of polymer-solvent interaction.

This paper deals with the effect of (a) solute concentration, (b) solvent type, and (c) temperature on number average molecular weight measurements by VPO for a series of binder prepolymers. Based on our studies we have concluded that molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results. For the determination of accurate

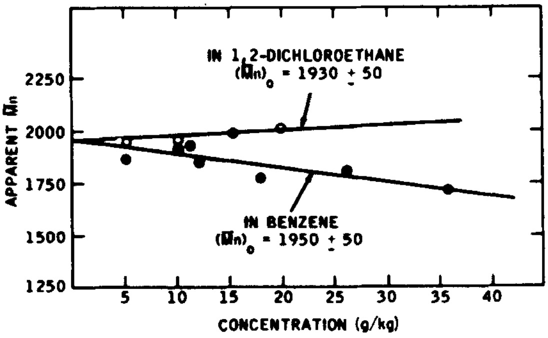

Fig. 1. Dependence of apparent molecular weight ($\overline{M}_n$) on concentration for Telagen-S, 242 AM-148 AH, in two different solvents at 37°C.

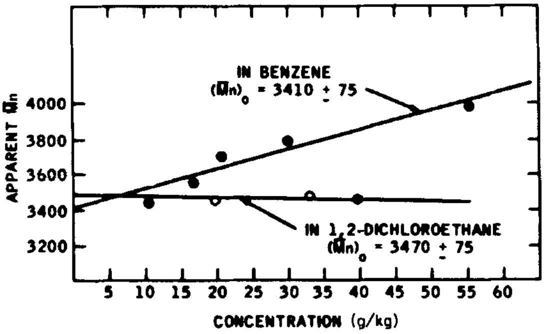

Fig. 2. Dependence of apparent molecular weight ($\overline{M}_n$) on concentration for P-BEP, 9088-180A, in two different solvents at 37°C.

number average molecular weights it is therefore important that apparent molecular weight measurements are extrapolated to infinite dilution [$(\overline{M}_n)_o$] to eliminate concentration effects.

The concentration dependence of number average molecular weight for several polymer-solvent-temperature systems is illustrated in Figs. 1-7. Figures 1 and 2 show the concentration dependence for an OH-terminated hydrogenated polybutadiene (OH-Telagen-S) and P-BEP, a hydroxy-functional prepolymer in two different solvents at 37°C, respectively. Molecular weight measurements at a single concentration level in either solvent would have been in error and the magnitude of the error would depend on 1) the slope of the concentration dependence and 2) the concentration level at which the measurement was made. The extrapolated molecular weights,

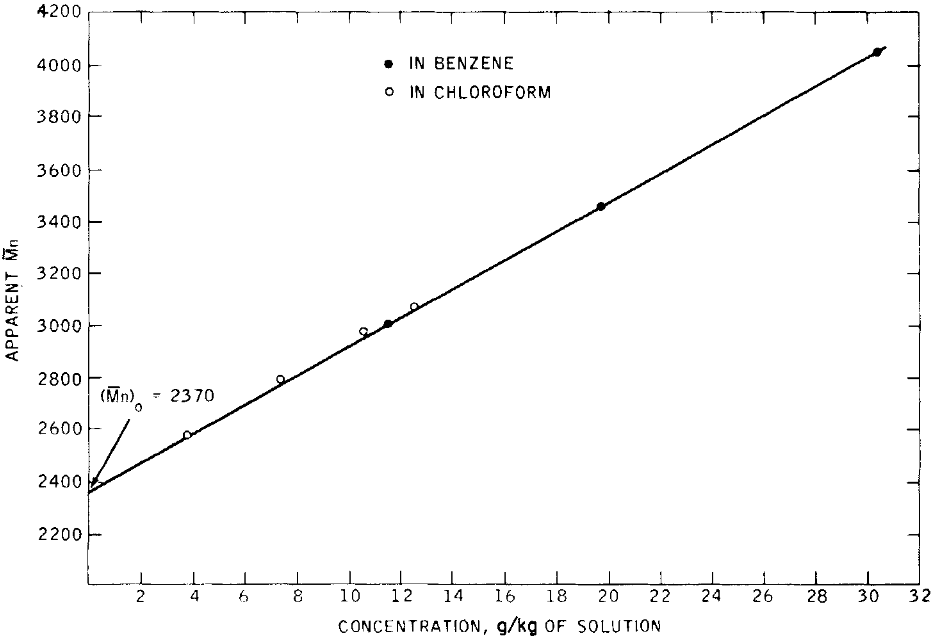

Fig. 3. Dependence of molecular weight, $\overline{M}_n$, on concentration for COOH-Telagen-S,242 AM 151 BH, in benzene and chloroform at 37°C.

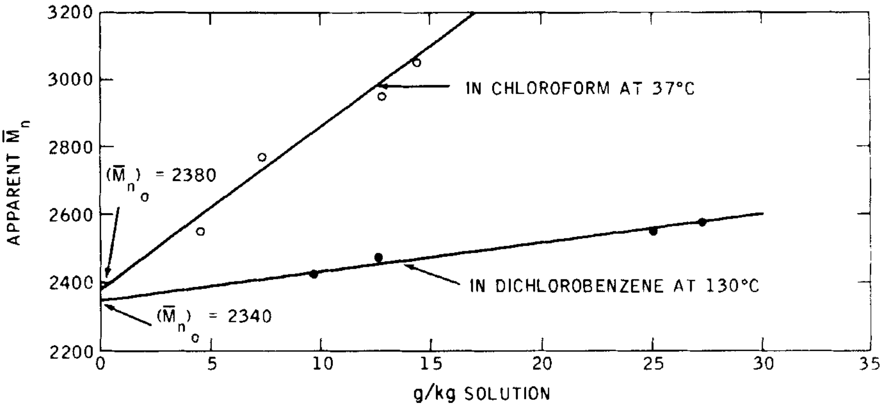

Fig. 4. Concentration dependence of molecular weight for COOH-Telagen-S, 242 AM 194 BH, in chloroform at 37°C and o-dichlorobenzene at 130°C.

$(\bar{M}_n)_o$, are in excellent agreement for the two solvents. The difference is only 1-2%. Figure 3 shows the concentration dependence for a COOH-terminated hydrogenated polybutadiene (COOH-Telagen-S) in benzene and chloroform at 37°C. Here is an example where the concentration dependence of a polymer is identical in two solvents. The very steep increase in molecular weight with increase in polymer concentration probably reflects polymer-polymer association through the carboxy-terminal groups. Figure 4 illustrates the concentration dependence for COOH-Telagen-S in two different solvents and at two different temperature levels. In chloroform at 37°C there is again the steep concentration dependence noted in Fig. 3. In o-dichlorobenzene at 130°C the concentration dependence has been greatly reduced; this probably reflects the effect of higher temperature level rather than differences due to the different solvents. The extrapolated molecular weights are again in excellent agreement, differing by less than 2%.

Figures 5-7 show the concentration dependence of molecular weight for a series of other COOH-functional prepolymers. They illustrate once again the different concentration dependences that are exhibited for different polymer-solvent systems. COOH-functional CNR-nitroso terpolymer shows a moderate positive slope in freon-215 at 37°C; the molecular weight increases with increase in concentration. The concentration dependence of molecular weight for COOH-polyisobutylene in o-dichlorobenzene at 130°C is essentially zero (Fig. 5) whereas COOH-Butarez shows a very pronounced negative slope in chloroform at 37°C and in o-dichlorobenzene at 130°C (Fig. 6).

Figure 8 illustrates a somewhat different point. It shows the concentration dependence of two Telagen-S fractions which had been isolated by

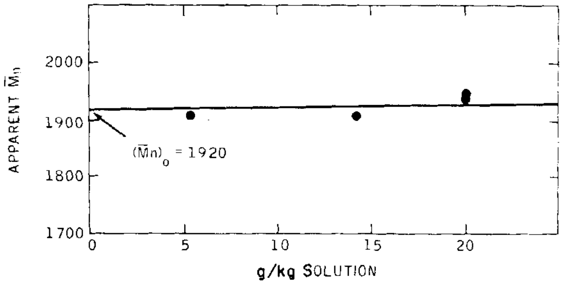

Fig. 5. Concentration dependence of molecular weight for COOH-polyisobutylene, EMD-590, lot CP_3 21-1, in o-dichlorobenzene at 130°C.

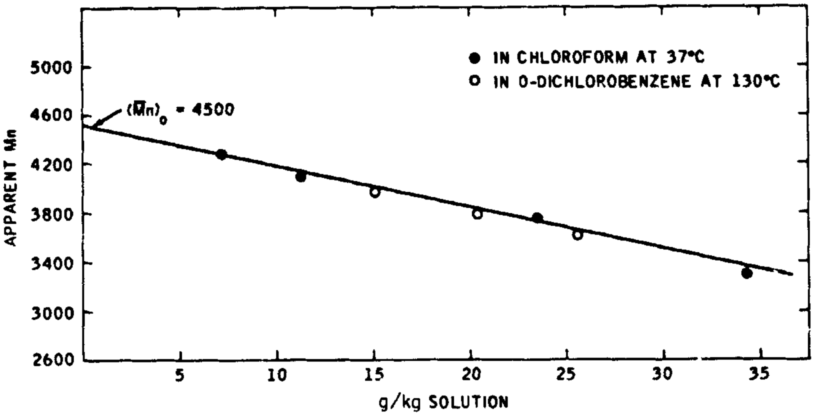

Fig. 6. Concentration dependence of molecular weight for Butarez CTL in chloroform at 37°C and o-dichlorobenzene at 130°C.

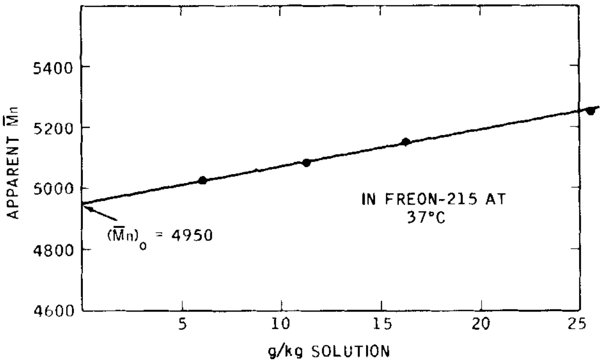

Fig. 7. Concentration dependence of molecular weight for CNR-nitroso terpolymer, lot A001-4D, in freon-215 (trichloropentafluoropropane) at 37°C.

fractionation. One fraction is a strictly difunctional COOH-terminated prepolymer; the other fraction is a strictly monofunctional COOH-prepolymer. It is interesting to note that the difunctional prepolymer has a much greater concentration dependence of molecular weight than the monofunctional prepolymer. This difference in concentration dependence probably reflects the extent of polymer-polymer association. The difunctional prepolymer can associate at both ends of the chain and would therefore give rise to an apparently higher molecular weight with increase in polymer concentration than the monofunctional prepolymer.

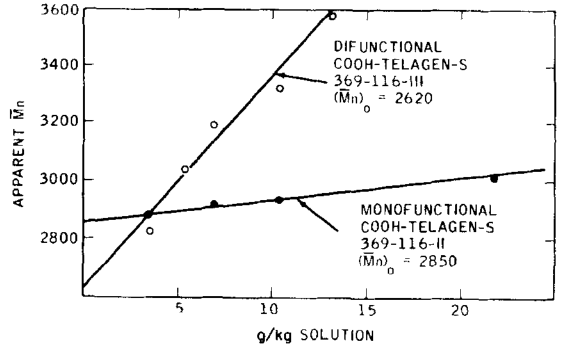

Fig. 8. Concentration dependence of molecular weight for mono- and difunctional COOH-Telagen-S in chloroform at 37°C.

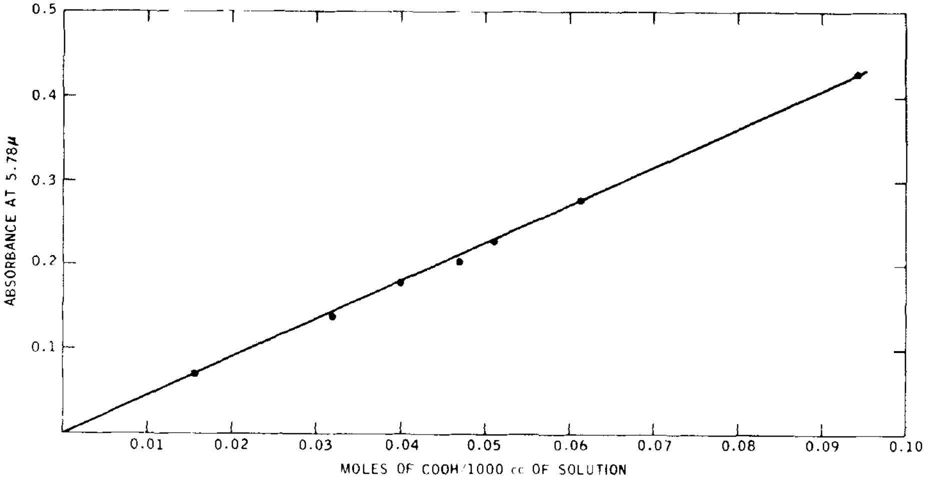

Fig. 9. COOH-calibration: stearic acid in tetrahydrofuran, 1c, 0.103 mm matched cells.

In conclusion, it should be stated that for the determination of accurate number average molecular weights it is very important that apparent molecular weight measurements are extrapolated to infinite dilution to eliminate concentration effects. Furthermore, the concentration dependence of molecular weight for a given polymer-solvent-temperature system cannot be predicted and must therefore be determined experimentally for each such system.

Equivalent Weight Determination

When fractionating prepolymers, small fractions of polymer need to be characterized with respect to molecular weight and equivalent weight. This does not represent a problem with respect to molecular weight measurements since existing methods inherently require only small samples. Conventional methods for equivalent weight determination, however, require large sample size (in the order of grams). There was, therefore, a need for small-scale equivalent weight methods which can accurately determine the equivalent weight of 50- to 100-mg polymer fractions. The method we have used in the case of COOH-functional prepolymers is based on measuring the intensity of the carbonyl absorption band at 5.7-5.8 μ in the infrared. A calibration is needed which relates the intensity of the carbonyl absorption band to the molar concentration of the calibrant. In selecting a suitable calibrant, two approaches are feasible: (1) Simulate the functional group of the prepolymer by using a carboxylic acid, such as stearic acid, as the calibrant. (2) An alternate method is to use the given prepolymer, whose equivalent weight has been accurately determined by base titration, as the calibrant. Figure 9 shows the correlation of carbonyl absorbance with molar concentration using stearic acid (● data points) and COOH-Telagen-S of known equivalent weight (line) as the calibrant. Both polymer and stearic acid gave the same identical correlation. The solvent (tetrahydrofuran) was chosen so as to prevent polymer-polymer association and to give a linear response of the intensity of the carbonyl absorption band with COOH molar concentration. The equivalent weight determination based on infrared absorption measurements is nondestructive and requires only small polymer samples. In practice, the equivalent weight of a polymer is determined by first determining the carbonyl absorbance of the polymer solution of known concentration and secondly reading from the calibration the molar concentration which corresponds to the particular absorption intensity.

The above method has also been applied to OH-terminated prepolymers by measuring the intensity of the hydroxyl band at about 2.8 μ. Butanol reference blends in a 25 vol% ethyl acetate/75% carbon tetrachloride solvent mixture were used to establish a linear calibration.

In the case of OH-functional prepolymers, we have developed a second, independent method for the determination of equivalent weight. The method is based on the reaction of the hydroxyl group of the prepolymer with p-toluenesulfonyl isocyanate, a very reactive isocyanate. The reaction is carried out in dilute solution at room temperature and is extremely

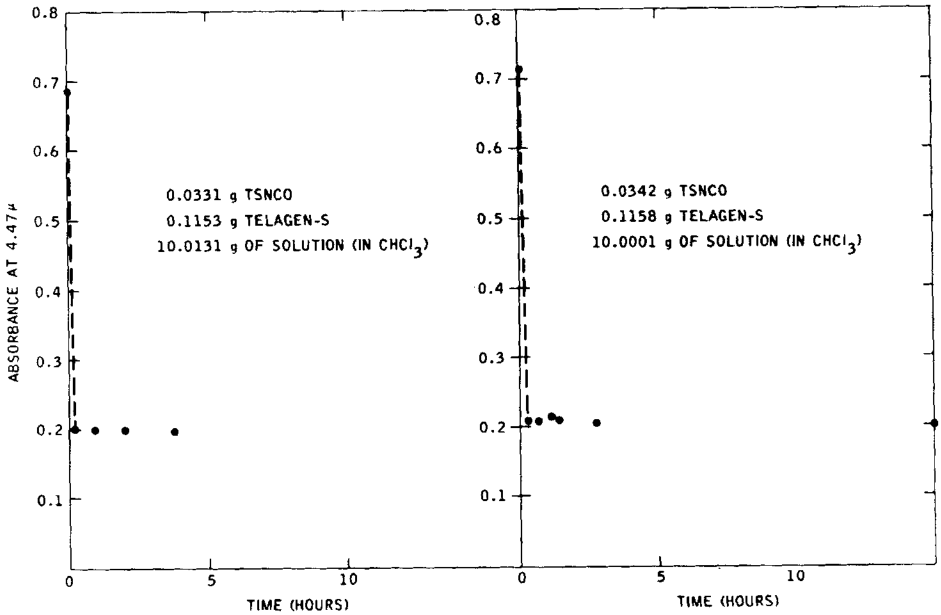

Fig. 10. Equivalent weight determination of OH-Telagen-S by reaction with excess p-toluenesulfonyl isocyanate in $CHCl_3$ at room temperature. Reaction monitored by infrared.

rapid [2, 3]. The isocyanate-hydroxyl reaction is monitored spectrophotometrically (infrared) by measuring the disappearance of the NCO stretching vibration at 4.4-4.5 μ. The feasibility of this method as an accurate, small-scale hydroxyl-equivalent weight method of prepolymers has been confirmed.

Figures 10 and 11 illustrate the method for two different OH-functional prepolymers. Figure 10 shows in duplicate the reaction of p-toluenesulfonyl isocyanate with a hydroxy-terminated, hydrogenated polybutadiene (OH-Telagen-S) at room temperature in chloroform. The reaction is very rapid and already complete at the time the first infrared scan is taken (about 15 min). The isocyanate absorbance at zero time is obtained from a calibration plot of the isocyanate. The equivalent weight is calculated from the amount of isocyanate that has reacted with a known amount of prepolymer. Figure 11 shows the corresponding reaction profile of P-BEP with p-toluenesulfonyl isocyanate. It is quite obvious from a comparison of Figs. 10 and 11 that the OH-group in P-BEP is less reactive than the OH group in OH-Telagen-S. Actually, it is not necessary to obtain the complete

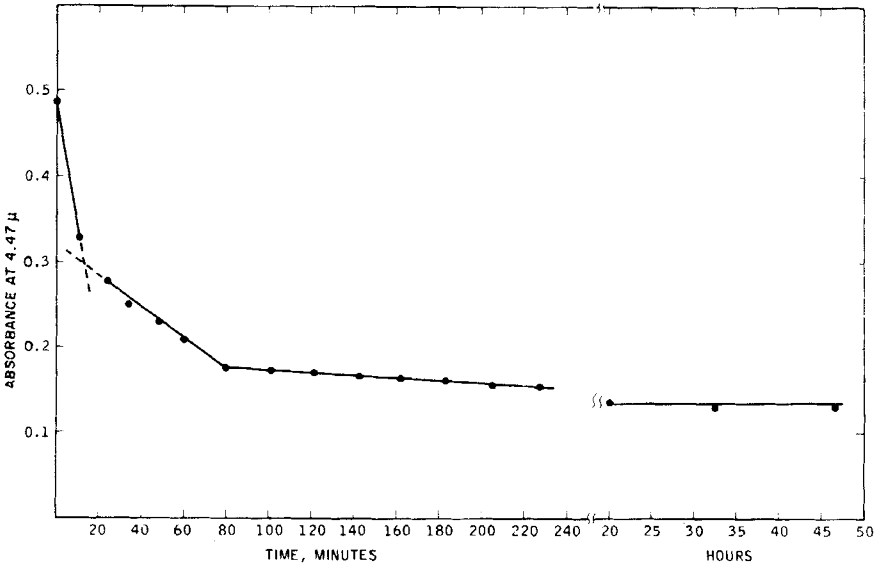

Fig. 11. Equivalent weight determination of P-BEP, 369-148, by reaction with excess p-toluenesulfonyl isocyanate in $CHCl_3$ at room temperature. Reaction monitored by infrared.

reaction profile; only the end point is needed to calculate the equivalent weight.

Functionality Distribution Measurements

Prepolymers do not in general have theoretical functionality. The determination of functionality distribution, that is, the percentages of non-, mono-, and difunctional polymer components, is therefore of particular importance, since functionality distribution will affect propellant mechanical properties.

The method we have developed to determine the functionality distribution of binder prepolymers is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono, and difunctional components. Nonfunctional polymer, which has no polar groups for adsorption by the silica gel, is eluted first from the column.

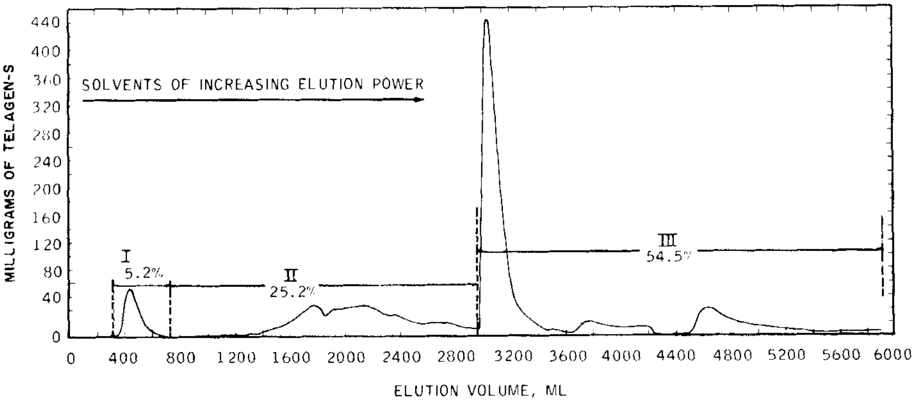

Fig. 12. Fractionation of OH-Telagen-S, 242 AM 148, by stepwise elution from silica gel. Silica gel/polymer ratio = 87/1. Elution profile.

FRACTION	WT % OF TOTAL	$(\overline{Mn})_o$	EQUIVALENT WEIGHT (GRAMS/OH)	FUNCTIONALITY
I	5.2	1780		0
II	25.2	2270	2240	1.01
III	54.5	1730	850	2.04
	84.9%			

Fig. 13. Functionality distribution of OH-Telagen-S, 242 AM-148 AH.

Monofunctional polymer, which is adsorbed on the column packing at one end of the polymer chain, is eluted next in response to a more polar solvent mixture. Difunctional polymer requires a progressively more polar solvent mixture to be desorbed, since it is adsorbed on the silica gel surface at both ends of the polymer chain. Based on the elution profile, individual polymer fractions are appropriately recombined into three or more major fractions and analyzed for functionality. Prepolymers which have been characterized by this technique include OH-terminated hydrogenated polybutadienes (OH-Telagen-S), COOH-terminated hydrogenated polybutadienes (COOH-Telagen-S), and COOH-terminated polyisobutylenes. Typical prepolymer samples analyzed to date contain 0-7% nonfunctional polymer, and 16-33% monofunctional polymer.

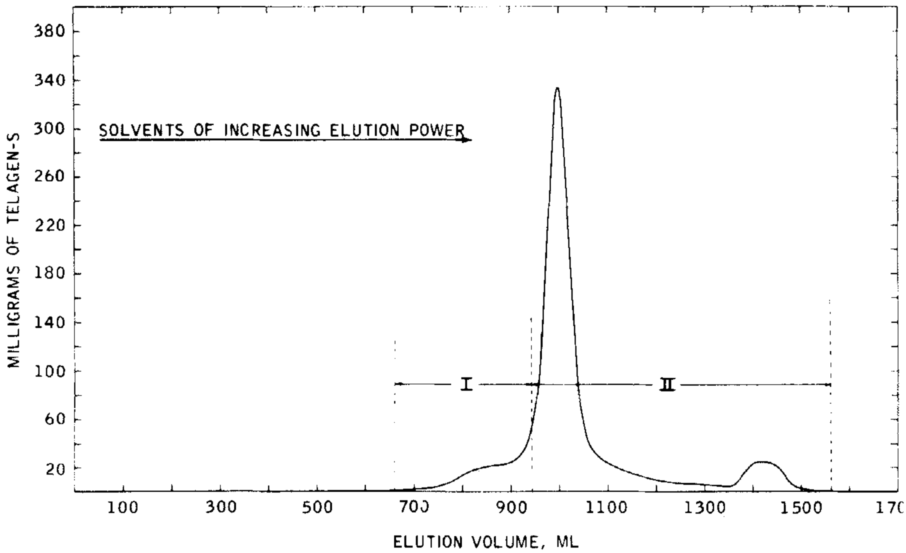

Fig. 14. Refractionation of difunctional OH-Telagen-S by stepwise elution from silica gel: elution profile.

FRACTION	WT % OF TOTAL	$(\overline{Mn})_n$	EQUIVALENT WT. (GRAMS/ MOLE OH)	FUNCTIONALITY
POLYMER CHARGED TO COL.	100.0	1650	830	1.99
I	22.6	1700	880	2.02
II	70.0	1530	760	2.01

Fig. 15. Refractionation of difunctional OH-Telagen-S by stepwise elution from silica gel: analysis of fractions.

Figures 12-21 summarize the results on the determination of functionality distribution for a number of OH- and COOH-terminated prepolymers based on the above-mentioned method. The respective elution profiles and analytical results on the functionality determination of the recombined polymer fractions are shown separately for each polymer sample.

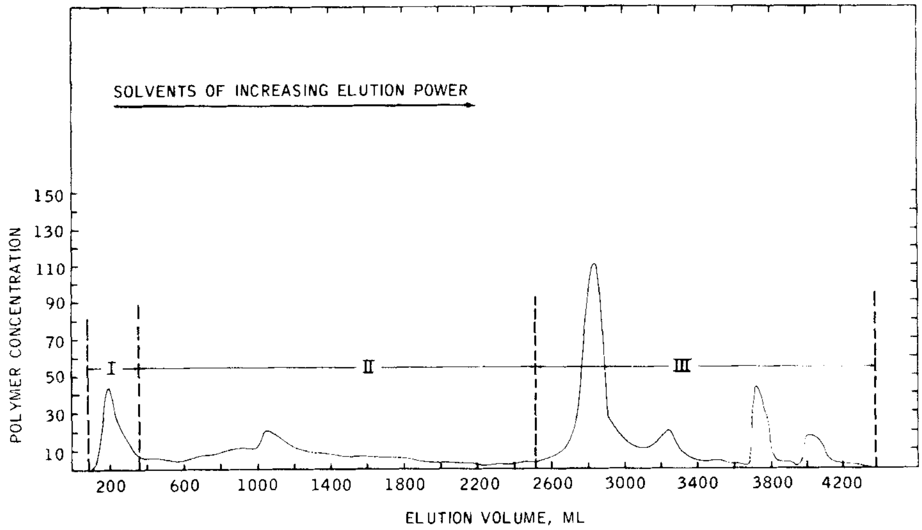

Fig. 16. Fractionation of COOH-Telagen-S, 242 AM 151 BH, by stepwise elution from silica gel. Silica gel/polymer ratio = 100/1. Elution profile.

FRACTION	WT % OF TOTAL	$(\bar{M}n)_o$	EQUIVALENT WEIGHT (GRAMS/OH)	FUNCTIONALITY
I	10.8	2550	6500	0.39
II	28.5	3000	3100	0.97
III	57.2	3000	1515	1.98

Fig. 17. Functionality distribution of COOH-Telagen-S, 242 AM 151 BH.

To assure that difunctional polymer was not converted to non- and/or monofunctional polymer on the silica gel column, we refractionated a difunctional OH-Telagen-S fraction and analyzed the eluted polymer. Figures 14 and 15 show the corresponding elution profile and analyses of the front and main fraction. The elution profile and analyses show conclusively that no conversion to non- or monofunctional polymer had taken place.

Figure 20 indicates in some detail a typical solvent composition and elution schedule that is used for COOH-functional prepolymers.

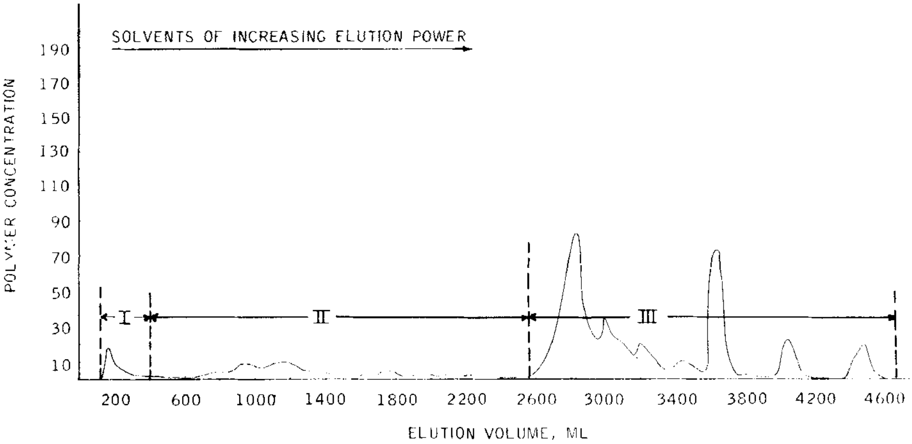

Fig. 18. Fractionation of COOH-Telagen-S, 242 AM 194 BH, by stepwise elution from silica gel. Silica gel/polymer ratio = 100/1. Elution profile.

FRACTION	WT % OF TOTAL	$(\bar{M}n)_o$	EQUIVALENT WT. (GRAMS/ MOLE COOH)	FUNCTIONALITY
I	3.3	--	8200	
II	15.3	2850	2830	1.0
III	73.6	2620	1318	1.99

Fig. 19. Functionality distribution of COOH-Telagen-S, 242 AM 194 BH.

In the case of the P-BEP prepolymer, this technique of fractionation was not applicable because decomposition takes place on the column. The polymer was fractionated instead by molecular weight using fractional precipitation to determine whether functionality was dependent on molecular weight. Figures 22 and 23 show the molecular weight distribution curve and correlation of functionality with molecular weight for P-BEP 9542-60B. Above a molecular weight of 2700 (78% of the polymer) there is no significant dependence of functionality on molecular weight.

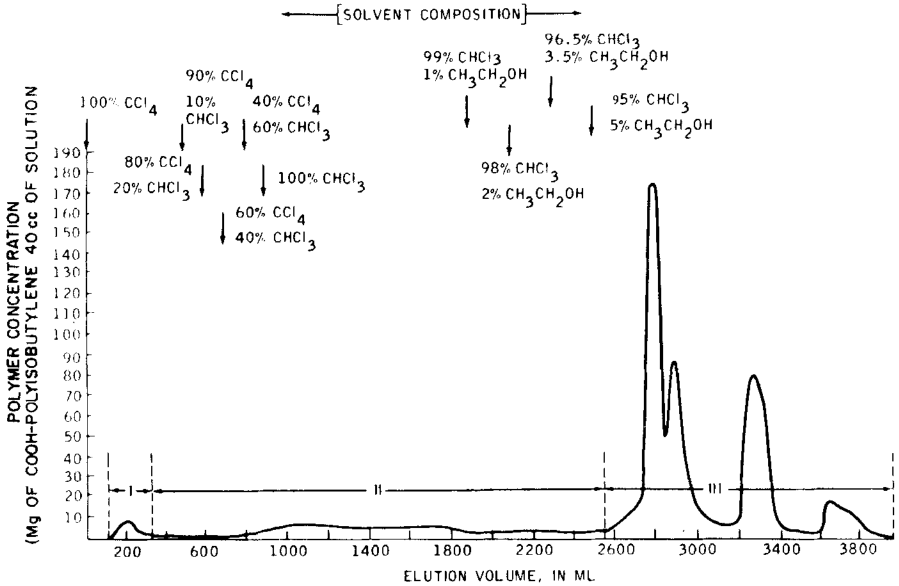

Fig. 20. Fractionation of COOH-polyisobutylene (CTPIB), EMD-590, lot CP_321-1, by stepwise elution from silica gel. Silica gel/polymer ratio = 118/1. Elution profile.

FRACTION	WT % OF TOTAL	$(\bar{M}n)_O$	EQUIVALENT WT. (GRAMS/ MOLE COOH)	FUNCTIONALITY
I	1.81	--	--	--
II	16.83	3300	3340	0.99
III	78.01	2040	1030	1.98
	96.65%			

Fig. 21. Functionality distribution of COOH-polyisobutylene, EMD-590.

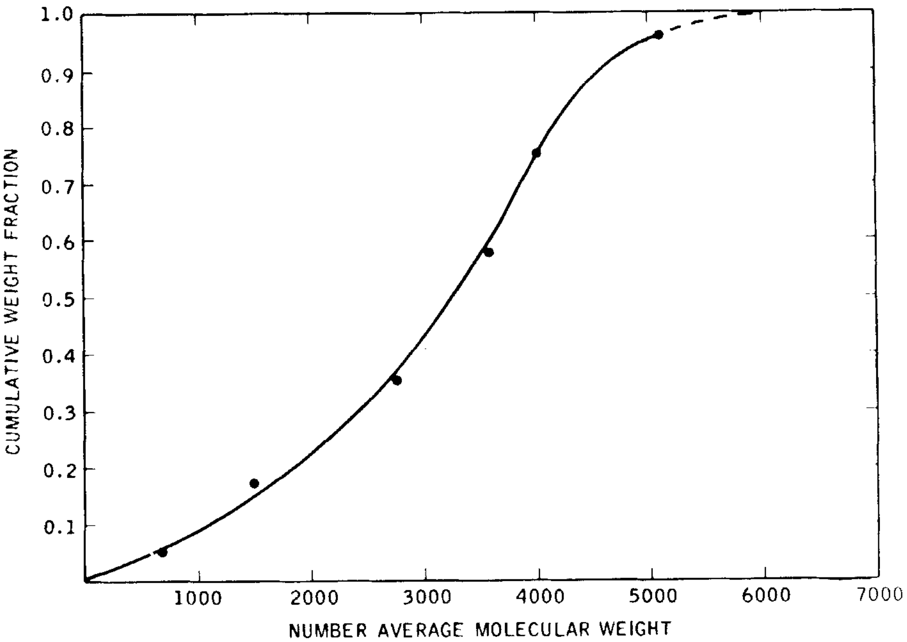

Fig. 22. Integral molecular weight distribution curve of P-BEP, 9542-60B.

In the low-molecular-weight range (1500 and below), however, there is a significant decrease in functionality, the functionality dropping below 1.0.

CONCLUSION

Molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results. For the determination of accurate number average molecular weights it is therefore important that apparent molecular weight measurements are extrapolated to infinite dilution $[(\bar{M}_n)_o]$ to eliminate concentration effects. The concentration dependence of molecular weight for a given polymer-solvent-temperature system cannot be predicted and must therefore be determined experimentally for each such system.

Carboxy- and hydroxy-functional prepolymers have been fractionated

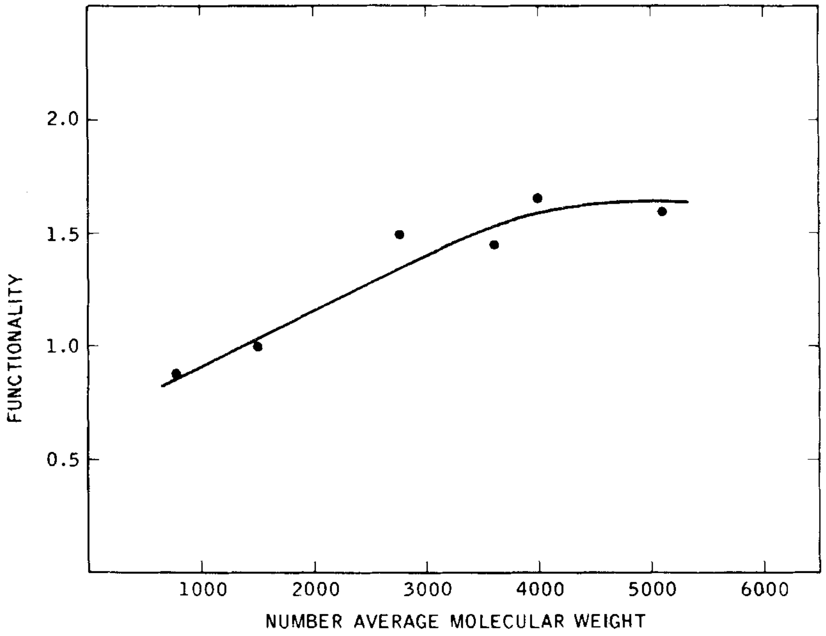

Fig. 23. Variation of functionality with molecular weight for P-BEP, 9542-60B.

by functionality by adsorption of the prepolymers on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power.

ACKNOWLEDGMENT

Research on functionality and functionality distribution measurements was sponsored by the Air Force and administered by Mr. Robert Corley and Lt. Raymond E. Foscante, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base.

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Accepted by editor May 27, 1969
Received for publication June 16, 1969

Discussion of Paper by Adolf H. Muenker and Boyd E. Hudson, Jr.

Functionality and Functionality Distribution Measurements of Binder Prepolymers

W. Kray:	Have you compared your number average molecular weight measurements by VPO with other conventional methods, such as ebullioscopic and cryoscopic measurements?
A. H. Muenker:	No.
R. F. Landel:	I would first like to compliment you on your very beautiful and very important piece of work. I have three questions: (1) Have you run any polyether-backboned materials such as polyoxypropylene? These are polar materials and hence might have different elution problems than those encountered with the hydrocarbon-backboned polymers you discussed. (2) Have you examined any polymer which has both primary and secondary hydroxyls (or carboxyls), and if so, can you see a difference in the fractionation behavior? (3) Could you comment on the accuracy of the analytical method as compared with some of the standard techniques? For example, in a hydroxyl analysis, mercuric acetate technique is the standard.
A. H. Muenker:	(1) We did not run any polyether except for P-BEP (a difluoroamino-containing polyether), which was in a category by itself. This material had special problems since it decomposed on the column. (2) No, we only examined polymers with secondary groups, but I suspect we would not see any difference. (3) We chose the toluene sulfonyl isocyanate method, which is accurate within 1-3%.