substrates to obtain sorption isotherms and hence to determine surface areas and enthalpies of adsorption. A primary requisite for this application is that bulk sorption into the polymer does not contribute to the retention of the adsorbate on the gas chromatographic column. Thus, only compounds having little tendency to dissolve in or swell the polymer in the time scale of the gas chromatographic experiment are useful as adsorbates. (Bulk sorption may also be reduced by working at column temperatures well below the glass-transition temperature of the polymer under study, where the rate of penetration is slower.)

Columns of relatively low internal surface area are necessary to avoid kinetic effects on peak shape which would invalidate the method used to calculate adsorption isotherms. In view of the low column area, and the resultant use of large, relatively nonvolatile adsorbate compounds, the agreement between the geometric surface areas of the polymers and the areas measured by the BET treatment of experimental isotherms is satisfactory. The use of relative peak retention volumes, measured at effectively zero coverage, provides an alternative and more rapid method of surface area determination. In this case, no restriction on the surface area of the column is necessary; in fact, as the specific surface area of the polymer is increased, the linear distribution region becomes more accessible and measurement of retention values becomes more accurate.

When a linear distribution region is accessible at low adsorbate concentrations, enthalpy data on adsorbate–polymer interactions may be readily derived from the variation in peak retention volumes with temperature. However, the results for *n*-hexyl alcohol on poly(methyl methacrylate) show that due allowance must be made for possible adsorbate–adsorbate interactions. When the distribution isotherms are nonlinear, the temperature dependence of the isotherm shape should in principle enable adsorption enthalpies to be calculated as a function of surface coverage. However, the accuracy of adsorption enthalpies calculated by this method from nonlinear isotherms appears unsatisfactory.

In general, a significant amount of information on the properties of polymer surfaces may be obtained by simple and rapid gas chromatographic experiments.

Acknowledgments. The authors wish to acknowledge the generous financial support of the National Research Council of Canada and of Dunlop Research Limited.

Molecular Weight–Intrinsic Viscosity Relationships for Phenol–Formaldehyde Novolak Resins[1a]

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ABSTRACT: Intrinsic viscosity and number-average molecular weight data have been determined for fractionated acid-catalyzed linear phenol–formaldehyde novolak resins. The Mark–Houwink expressions for the fractionated phenol–formaldehyde polymer in acetone, DMF, and 1 *N* NaOH at 25° were found to be $[\eta] = (1.90 \times 10^{-3})M^{0.47}$, $(1.80 \times 10^{-3})M^{0.51}$, and $(1.66 \times 10^{-3})M^{0.48}$, respectively, for a molecular weight range of 1000–8000. The log [η]–log *M* plot curves upward below 1000, similar to a number of other low molecular weight polymers which have recently been studied. The unperturbed end-to-end chain dimensions were estimated by the Flory–Fox method to be $0.88M^{1/2}$ Å. For the unfractionated parent polymer, a molecular weight ratio M_w/M_n of approximately 2.3 was found, with M_w and M_n in the region of 2100 and 900, respectively. Solvent behavior in formamide, ethyl acetate, methanol, and NaOH showed interesting effects on the Mark–Houwink data, not only through curve displacement, but also by shifting the position of the low molecular break in the curve. Variation in the Mark–Houwink parameter *a* from 0.51 in DMF to 0.24 in formamide is examined in terms of chain coil compactness.

Polymers formed by the reaction of phenol and formaldehyde under varied mole ratios and either acid or base catalyst conditions produce interesting and useful materials. The materials which are described here are called novolaks, since they are prepared with a mole ratio of phenol to formaldehyde greater than one and under acid conditions. A typical structure is shown in Figure 1. The linkages are distributed between ortho and para positions,[2] and form what might be considered a flexible linear polymer system. On the other hand, if the polymerization is carried out in a basic medium with the phenol to formaldehyde mole ratio less than one, resoles are formed that are branched and have reactive methylol end groups.

This viscosity–molecular weight study on linear novolak structures was undertaken to formulate a model which would be useful in interpreting properties such as stiffness, branching, and molecular weight distribution in the more complicated resole structures.[3] This system also proves to be a novel one in which to study the dilute-solution properties of low molecular weight materials which have drawn attention recently.[4–6] Present theory predicts that viscosities should decrease rapidly as low molecular weights are approached, but this is not generally observed experimentally.

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(1) (a) Part of the material was presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 1101 (1970). (b) Pacific Lutheran University. (c) Reichhold Chemicals.

(2) (a) A. A. K. Whitehouse, E. G. K. Pritchertt, and G. Barnett, "Phenolic Resins," Elsevier, New York, N. Y., 1968; (b) W. Martin, "The Chemistry of Phenolic Resins," Wiley, New York, N. Y., 1956, pp 107–109.

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(5) L. S. Sandell and D. A. I. Goring, *Macromolecules*, **3**, 50 (1970).

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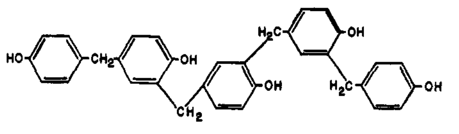

Figure 1. Representation of novolak phenol–formaldehyde oligomer.

TABLE I
INTRINSIC VISCOSITIES (ACETONE, 25°), MOLECULAR WEIGHTS, AND PHENOL CONTENTS OF STARTING SAMPLES

Sample	$[\eta]$,[a] dl/g	M_n[a]	Wt % free phenol
E	0.069	680	4.0
G	0.065	730	3.8

[a] Not corrected for free phenol content.

Although a melt viscosity–molecular weight study for nonfractionated resins[7] and a gel permeation study[8] have been made, no dilute-solution viscosity correlation has been reported for this system.

Experimental Section

Sample Preparation. Two samples having a phenol to formaldehyde mole ratio of 6/5 were prepared from 99+ % commercial phenol and ion-exchanged (low formic acid content) 50% water solution of formaldehyde. The novolak prepared with reagent grade *p*-toluenesulfonic acid at pH 0.8 is labeled sample E, and the other sample prepared with reagent grade hydrochloric acid at pH $\simeq$0 is labeled sample G. The reactions were continually mixed and held at 90° for 4.5 hr. The system was considered to be the dimer plus any higher oligomer, with the reactants considered as impurities. Samples were vacuum dried at 50° before being used.

Fractional Precipitation. Samples G(2) and E(2) were fractionally precipitated at a constant temperature (±0.05°) from a 4% methanol solution with water as a nonsolvent. E(3) was fractionated after the sample had been steam distilled, and E(4) was precipitated from methanol after the sample had been plunged into water adjusted to a pH of 4 with oxalic acid. Each fraction collected was washed, vacuum dried, and weighed. In some cases as much as 6% by weight of the original sample was lost, primarily due to the phenol and some dimer. Number-average molecular weights and intrinsic viscosities of every sample were determined.

Viscosity Measurements. Flow times were measured using Cannon-Ubbelohde dilution viscometers at a constant temperature of 25 ± 0.03°. The ratio of solution to solvent flow time was between 1.1 and 1.5, and the time reproducibility was 0.1 sec. Baker analytical reagent grade acetone, *N,N*-dimethylformamide, methanol, ethyl acetate, and formamide were used as solvents. A 1 *N* solution of analytical grade sodium hydroxide was used for an aqueous solvent of high ionic strength, and also because these polymers may be used commercially in NaOH solutions. Intrinsic viscosities in deciliters per gram were determined by a least-squares extrapolation of η_{sp}/c from the Huggins equation and $(\ln \eta_r)/c$ to zero concentration,[9] yielding values of $[\eta]$ that agreed with each other to 1.5%.

Molecular Weights. Number-average molecular weights were determined using a Mechrolab Model 302A vapor pressure osmometer operating at 37.5°C with acetone for the solvent. Calibration standards used were poly(tetramethylene oxide) glycol (900), poly(ethylene oxide) glycol (425), and benzoic acid. Molecular weights are generally reliable to 1%.

TABLE II
FRACTIONATED NOVOLAK VISCOSITY AND MOLECULAR WEIGHT DATA

Sample	M_n(vpo)	$[\eta]$, dl/g	Huggins *k*
	Dimethylformamide		
E(3-1)	6150	0.172	0.56
E(3-2)	5840	0.122	1.16
E(3-3)	4900	0.120	0.74
E(3-4)	2750	0.103	0.64
G(2-2)	4250	0.130	1.50
G(2-3)	3560	0.119	0.69
G(2-7)	1320	0.066	1.06
G(2-8)	660	0.053	0.92
Bisphenol	200	0.035	0.98
Phenol	94	0.017	0.23
	Acetone		
E(2-5)	3840	0.090	0.75
E(2-7)	2860	0.078	0.88
E(2-8)	2470	0.070	0.91
E(2-9)	1870	0.064	0.70
E(2-10)	1740	0.059	0.57
E(2-11)	870	0.051	0.76
E(2-12)	420	0.043	0.96
E(3-1)	6150	0.119	0.80
E(3-2)	5840	0.106	0.77
E(3-3)	4900	0.087	0.97
E(4-1)	8050	0.119	0.92
E(4-2)	6000	0.106	0.73
G(2-2)	4250	0.103	0.85
G(2-3)	3560	0.086	0.82
G(2-4)	2730	0.073	0.83
G(2-5)	2900	0.073	0.84
G(2-6)	1880	0.063	0.93
G(2-7)	1320	0.055	0.88
G(2-8)	660	0.047	0.72
Bisphenol	200	0.031	0.83
	1 *N* NaOH		
E(3-3)	4900	0.095	1.40
G(2-6)	1880	0.060	1.34
G(2-7)	1320	0.051	1.03
G(2-8)	660	0.039	1.75
Bisphenol	200	0.035	1.22
Phenol	94	0.025	0.93
	Ethyl Acetate		
E(3-3)	4900	0.084	1.08
G(2-6)	1880	0.059	1.22
G(2-7)	1320	0.052	1.30
G(2-8)	660	0.045	1.30
Bisphenol	200	0.035	0.82
	Methanol		
E(3-3)	4900	0.071	0.88
G(2-6)	1880	0.055	0.88
G(2-8)	660	0.041	1.07
Bisphenol	200	0.029	0.99
	Formamide		
E(3-3)	4900	0.056	0.39
G(2-6)	1880	0.044	0.83
G(2-7)	1320	0.041	0.74
G(2-8)	660	0.037	1.10
Bisphenol	200	0.027	0.96

Ir Work. The amount of phenol present in the samples was determined using a Perkin-Elmer 457 ir spectrophotometer. The monosubstituted aromatic ring band at 698 cm^{-1} was used for the Beer's law determination.

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[7] T. T. Jones, *J. Appl. Chem.*, **2**, 134 (1952).

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Results

The Huggins curves were all linear, indicating that a polyelectrolyte effect was not operating in the organic solvents or in the 1 N sodium hydroxide solution. Table I lists some basic data on samples E and G. The intrinsic viscosity and the molecular weight have a high dependence on the phenol content present in these samples. The viscosity increases with increasing phenol content owing to its effect on polydispersity and because it acts as a diluent. Consequently, the bulk sample intrinsic viscosity is much higher than the viscosity of a fraction with the same molecular weight.

Table II lists the molecular weight, intrinsic viscosity, and Huggins' constant data for fractionated samples. There was no detectable free phenol present in the fractions, except for sample E(2-12). The Huggins constants are included for comparison, even though they are not used directly in this work. The intrinsic viscosity–molecular weight data for fractionated samples in acetone are illustrated by the Mark–Houwink plot in Figure 2. These fractionated samples should have a narrow distribution and, therefore, using the number-average molecular weight for the weight-average molecular weight in the Mark–Houwink equation should be valid. The reproducibility of data from samples handled in different ways would indicate that the fraction polydispersity was the same. The upward break found in this curve at about an M_n of 1000 is of special interest. Figure 3 illustrates the log [η]–log M_n plot for the fractionated phenol–formaldehyde oligomers in DMF. The Mark–Houwink data for the fractionated polymer in ethyl acetate, methanol, formamide, and 1 N NaOH are illustrated in Figure 4. Table III summarizes the K and a Mark–Houwink parameters (refined by least squares for the data above M_n = 1000) for the resins in the various solvents and correlates these values with the dielectric constant, and $[\eta]_{E(3\text{-}3)}$, for that medium.

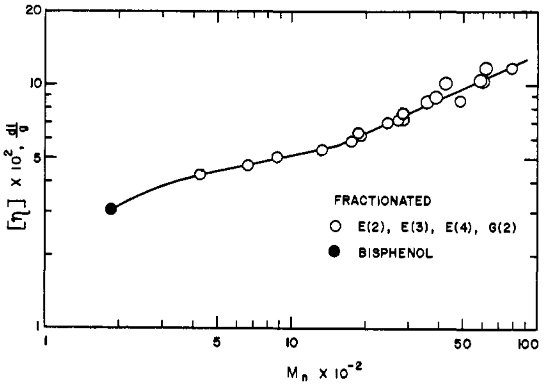

Figure 2. Mark–Houwink plot for fractionated phenol–formaldehyde resins in acetone.

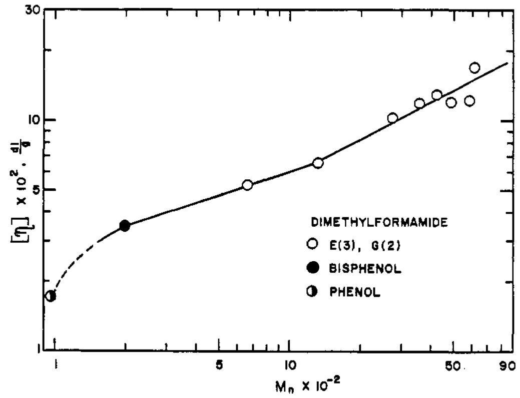

Figure 3. Mark–Houwink plot for fractionated phenol–formaldehyde resins in DMF.

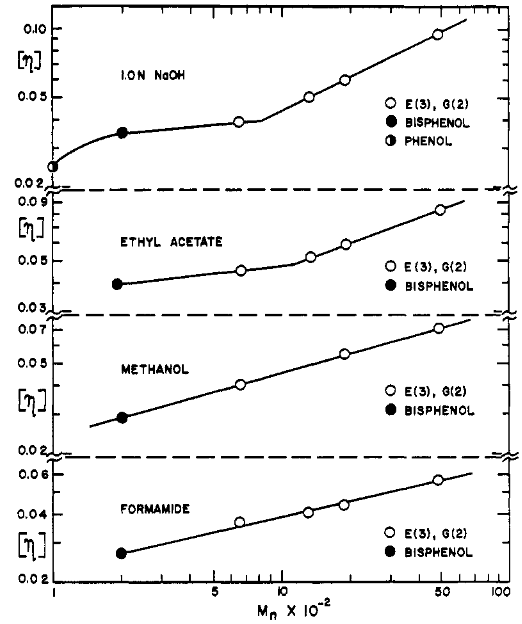

Figure 4. Mark–Houwink plots illustrating solvent dependence of fractionated phenol–formaldehyde resins.

Table III

Comparison of Solvent Dielectric Constant, Intrinsic Viscosity for Fraction E(3-3), and Mark–Houwink Parameters at 25°

Solvent	a	$K \times 10^3$, dl/g	ϵ^a	$[\eta]_{E(3\text{-}3)}$, dl/g
Dimethylformamide (DMF)	0.51	1.80	37.0	0.120
1 N NaOH	0.48	1.66	78.5	0.095
Acetone	0.47	1.90	20.7	0.087
Ethyl acetate	0.38	1.13[b]	6.0	0.084
Methanol	0.28	6.61[b]	32.6	0.071
Formamide	0.24	7.20[b]	105.4	0.056

[a] Dielectric constants are from A. Maryott and E. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951. [b] These values are not structurally meaningful according to theory.

The a values are nearly 0.5 for the first three solvents, which allows the unperturbed molecular chain dimensions to be estimated by the Flory method, assuming Θ conditions are simulated and assuming that the low a values are not caused by branching effects. The Flory–Fox equation relates the K values of the Mark–Houwink relationship to the root-mean-square end-to-end chain distance parameter, $(\overline{r_0^2})^{1/2}$, by $K = \phi(\overline{r_0^2}/M)^{3/2}$, where the Flory constant, ϕ, is approximated as 2.60×10^{21} for a well-fractionated polymer.[10] The average K value from the acetone, DMF, and NaOH data is 1.79 $\times 10^{-3}$ dl/g. The estimated unperturbed root-mean-square end-to-end distance is $0.88M^{1/2}$ Å.

Figure 5 illustrates the differential distribution curve for

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(10) J. Brandrup and E. H. Immergut, "Polymer Handbook," Interscience, New York, N. Y., 1966, Section IV-5.

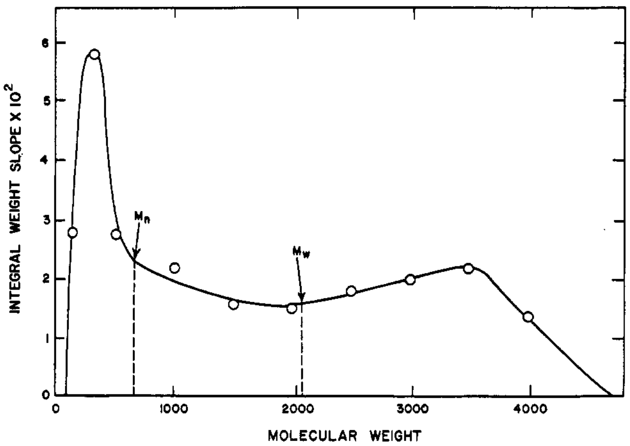

Figure 5. Differential distribution curve constructed from fractionation data for sample G.

TABLE IV
MOLECULAR WEIGHT DISTRIBUTION DATA

Sample	M_n(calcd)[a]	M_w(calcd)	M_n(exptl)[b]	(M_w/M_n) (calcd)
E	908	2095	677	2.3
G	938	2089	730	2.2

[a] Including the 4% phenol brings this in line with the bulk sample value. [b] Taken on sample lightly washed and still containing approximately 4% phenol as shown by ir.

sample G constructed from the fractionated sample data, and Table IV summarizes the important molecular weight parameters. The number- and weight-average molecular weights calculated from the fractionated sample data are in agreement with those reported by Gardikes and Konrad,[8] as is the general shape of the distribution curve. The shape of this distribution curve, however, indicates that a bimodal distribution is present. A curve similar to Figure 5 was obtained for sample E. The calculated M_n is higher than the experimental M_n of the bulk sample by an amount which can be accounted for by the per cent free phenol present.

Discussion

Mean-Square End-to-End Dimensions. In correlating viscosity and molecular weight measurements at low molecular weights, it becomes a real problem to know whether or not the theoretical equations that are used for larger molecular weights are valid. Theory as derived by Kirkwood and Riseman[11] predicts that as short chains are approached, the viscosity should drop off rapidly with a molecular weight dependence to the first power. Rossi and Perico[12,13] extended this theory by accurately taking into account short-chain behavior. They concluded that the free-draining effects were overweighted in the Kirkwood–Riseman theory and calculated less of a viscosity drop off with decreasing molecular weight. They also concluded that molecular weights could be interpreted by high polymer theory down to a very low range. However, experimental results[4,5] generally show the viscosity turning up as some low critical molecular weight (500–5000) is approached.

Bianchi and Peterlin[4] conclude from their work on short-chain polymers that the Mark–Houwink data, even in a non-Θ solvent, turns up and passes through a region where $a = 0.5$ and that unperturbed molecular dimensions can be deduced from the intercept K of this linear portion of the curve. It is felt that these novolak molecular chains in DMF and acetone ($a = 0.5$) represent a Gaussian system and that the Flory–Fox equation can be applied to yield an estimate of the unperturbed molecular dimensions. The conditions, however, may not be true Θ conditions. The root-mean-square end-to-end dimensions, $0.88M^{1/2}$ Å, are not unreasonable when compared to measurements made from molecular models of linear o/p novolaks placed in different conformations. Chain configuration calculations based on the rotational isomeric state model are also in progress to check this.

Another concern when interpreting these results is the possibility of branching in the novolaks. This appears conceivable when looking at the chemistry. However, when prepared by the method stated, this is supposed to be minimal.[2] Furthermore, branching would be expected to increase with increasing molecular weight, and the viscosity should decrease with increased branching.[14] The Mark–Houwink plots should then show curvature downward with increasing molecular weight, which they do not. Although it is possible that a few short branches may not affect the data, or that the molecular weight span was too small for this effect to show up, we conclude that branching is not playing a significant role in the data from these novolaks. The Mark–Houwink parameters for the fractionated novolaks listed in Table III for the solvents DMF, acetone, and 1 *N* NaOH should be valid.

Solvent Interaction and Molecular Chain Compaction. It is of interest to find in this study an upward turn in the Mark–Houwink plot with decreasing molecular weight. This is similar to that observed in PEOG and PPOG.[4] There appears to be a critical molecular weight region where this happens, and it is definitely a function of the molecular structure and the nature of the solvent medium, and probably a function of the temperature. In the novolak fractions examined, an upward break is found in acetone, DMF, 1 *N* NaOH, and ethyl acetate at a molecular weight around 1000. This break is not observed in the formamide or methanol mediums. In Figures 2, 3, and 4 it is important to note the consistency of the data as checked by independently evaluating the viscosity of bisphenol, the most likely dimer. It falls basically on the extrapolated curves. The phenol viscosity point is included because it represents the simplest unit that the small chains must pass through in an extrapolation to zero molecular weight. Its sharp decrease in viscosity is noteworthy.

The Mark–Houwink slope is very small in the solvents formamide and methanol, and since there is no apparent break in the curve, one must conclude that the critical upturn point in these solvents is above a molecular weight of 5000. It is also apparent that a special solvent effect must be operating. We generally find a greater solvent dependency than Bianchi and Peterlin[4] would predict for short chains.

First consider the molecular weight region above 1000 in the Mark–Houwink curves. Table III shows how the slope a varies with dielectric constant and also how it correlates with the viscosity of the E(3-3) fraction. There is reason to believe that the dielectric constant can be related to chain coil

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(11) G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).
(12) C. Rossi and A. Perico, *ibid.*, **53**, 1217 (1970).
(13) A. Perico and C. Rossi, *ibid.*, **53**, 1223 (1970).
(14) M. L. Miller, "The Structure of Polymers," Reinhold, New York, N. Y., 1966, pp 123–136.

expansion,[6] but no consistent correlation was found in this study. The methanol and formamide data appeared out of line because of the drop in a and viscosity. This, however, could be due to a special solvent effect. A consistent correlation of a with the intrinsic viscosity of fraction E(3-3) is observed. There is a rapid decrease in a found with decreasing $[\eta]_{E(3\text{-}3)}$, being lowest in formamide. If the polymer behaved like an Einstein sphere in a particular solvent, the exponent a in the Mark–Houwink equation would be zero and the intrinsic viscosity would be lower than the expanded non-free-draining coil for that polymer. Consequently, we conclude that the novolak polymer chains range from a fairly compact sphere (probably more ellipsoidal) in formamide to those behaving like normal Gaussian coils in DMF. The chains are probably acting as tightly compact structures in formamide and methanol because of the very strong intramolecular hydrogen bonding present in these compounds. In these media solvent–polymer interactions would be small, which leads to methanol and especially formamide acting as poor solvents. In the other solvents, strong intermolecular hydrogen-bonding interactions are possible, being strongest for DMF, and this allows the polymer chains to take on an expanded Gaussian form. The latter apparently approaches a model much like that expected in a Θ solvent. The NaOH data are considered explicitly in this discussion because the NaOH solution mechanism is an ionic one.

The above rationale seems like a reasonable explanation of the general trends, but does not necessarily explain exactly what is influencing the break in the Mark–Houwink curves below a molecular weight of 1000. The slope of the lower portion of the novolak curves in acetone and DMF is about 0.22, which compares to 0.24 for low molecular weight poly(propylene oxide) glycol in H_2O[5] and 0.28 in poly(ethylene oxide) glycol.[4] These are nearly the same as found for the novolaks in formamide and methanol. Although it varies with solvent and the shortness of the molecular chains, many polymers appear to have this Mark–Houwink slope behavior. It is possible that in DMF and acetone a molecular weight is reached where the polymer chains change from a random coil to a compact structure as they appear to be in formamide over a wider molecular weight range. However, if this were true, one might ask why the viscosity of low molecular weight novolaks in acetone does not show a sharp decrease instead of an increase. The viscosity upturn with decreasing molecular weight has been partly taken into account by including the importance of chain thickness relative to the mean-square chain dimensions as low molecular weight chains are approached,[13] or by considering how the smallest unit in a flexible chain of beads influences the chain viscosity.[4] Both of these methods are based on a flexible coil and hence do not seem consistent with the compact structure ideas discussed here or found in poly(propylene oxide) glycol.[6] The equivalent ellipsoid model would seem more appropriate in the low a region of the viscosity curves.

Study on the Distribution of Dyads in Acrylonitrile–Methyl Acrylate Copolymers by Pyrolysis Gas Chromatography

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ABSTRACT: The distribution of dyads in acrylonitrile–methyl acrylate copolymers has been studied by means of pyrolysis gas chromatography (pgc). A cluster of dimer peaks appearing on the pyrograms has been identified by a mass spectrometer combined with pgc and interpreted in terms of the dyad distributions in the copolymers. The experimentally estimated concentrations of dyads were in fair agreement with those calculated from copolymerization theory over a wide range of composition of the copolymers.

Acrylonitrile (AN)–methyl acrylate (MA) copolymer is one of the most intractable copolymers to characterize with respect to microstructure. Although nmr can provide some information related to the monomer distribution of copolymers such as vinylidene chloride–isobutylene[1] and styrene–methyl methacrylate,[2] the spectra of the AN–MA copolymer are not sufficiently characteristic to make quantitative interpretation of the microstructures possible.

In our previous work,[3,4] pyrolysis gas chromatography (pgc) was successfully used for the first time to determine the quantitative concentration of the triad sequences in vinylidene chloride–vinyl chloride copolymers. Although some studies on the characterization of AN–MA copolymer have been reported by means of pgc, none have succeeded in obtaining quantitative data concerning the monomer distribution. Wall[5] and Shibasaki,[6,7] however, have already suggested that the boundary effects of the pyrolysis of the copolymer which will affect the formation of hybrid monomers provide good information about the monomer distribution.

In this paper, the concentrations of dyads in the copolymers have been experimentally estimated utilizing the cluster of dimer peaks appearing on the pyrograms of AN–MA copolymers by means of pgc. The identification of the dimer peaks was carried out by combining pgc directly with a mass spectrometer (ms). The observed dyad concentrations were successfully compared with those calculated from the copoly-

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