

# Kinetics of Polycondensation of Urea with Formaldehyde. Molecular Weight Distribution, Average Molecular Weight, and Polydispersity Parameters

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## Synopsis

The molecular weight distribution, molecular weight averages  $\overline{M}_n$ ,  $\overline{M}_w$ ,  $\overline{M}_z$ , polydispersity coefficient, statistic standard deviation of number and weight distribution, and Hoseman-Schramek index of the polycondensates of urea with formaldehyde have been estimated. The properties of this solution were obtained by the help of the combination of the following methods: GPC, VPO, turbidimetric titration, and fractional precipitation. The course of the polycondensation described was formally divided in the following stages: (1) formation of methylolated urea derivatives and of the lowest oligomers, (2) decrease in the content of methylol urea and in the content of the lowest oligomers with  $M < 200$ , and production of soluble molecules between  $10^3$  and  $10^4$ , and (3) formation of insoluble products.

## INTRODUCTION

Functional groups and linkages of urea-formaldehyde (UF) polycondensates are not very stable; relatively careful methods commonly used in analytical chemistry may provide distorted results.

Methods for separation and identification of the low-molecular fractions of UF resins or initial reaction products formed during the formaldehyde resin production have been well worked out. The most appropriate procedures for studying molecular weight distributions of UF adhesives including higher molecular weight fractions are liquid and mainly gel permeation chromatography. Greatest difficulties encountered in the study of the UF thermosetting resins by the GPC method are caused by the low solubility of some fractions of polycondensates, their chemical and thermal lability, hygroscopicity of dry samples, and unavailability of monodisperse standards of UF resins or thermosetting resins of a similar structure.

Aldersley et al.<sup>1</sup> and Armonas<sup>2</sup> have shown that the GPC analysis of UF polycondensates does not give as good a separation as can be obtained in fractionation of phenolformaldehyde or melaminoformaldehyde resins. They present envelope elution curves of some samples of UF resins. The authors have not reported on the calibration of the chromatograms obtained.

Tomáš, Katuščák, and Schiessl<sup>3</sup> studied commercial and laboratory preparations of UF resins using the pressure GPC system on the columns: Porasil A, 120 cm, Porasil B, 120 cm, Sephadex LH-20, 60 cm, in solvents: dimethyl sulfide, dioxan with 40 and 50% water; THF with 10% water. Solvent systems were chosen according to the study of the solubility of the UF resins (Aerolite, Ciba;

Cascamite, The Borden Chem. Co; Diakol S, Diakol M, Diakol F, Chemko, Czechoslovakia; Umakol C, VCHZ, Czechoslovakia; fraction of laboratory prepared resin with  $\bar{M}_n = 2030$ ) in the following solvents: water, tetrahydrofuran (THF) with 5, 10, and 20% water; dimethyl formamide (DMF) with 5, 10, and 20% water; dioxan 10, 20, 30, 40, and 50% water; 85% formic acid;  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , methanol, ethanol, *n*-propanol, isopropanol, and acetone. Urea derivatives prepared by repeated fractional precipitation were used for calibration. It was found that polystyrene (PS) and poly(ethylene glycol) (PEG) standards in the GPC system cannot be employed for the investigation of UF resins. The values of  $\bar{M}_n$  for the commercial UF adhesives were found to range between 200 and 500 and  $\bar{M}_w$  between 300 and 1500.

Hope et al.<sup>4</sup> found by GPC that a considerable number of molecules of UF resins are of effective size corresponding to the molecular weights greater than 1100.

Tsuge and co-workers<sup>5</sup> investigated number- and weight-average molecular weights in an open column by descending gel chromatography on Sephadex LH-20, 80 cm, in DMF. Urea, mono- and dimethylol urea, methylenediurea, dimethylol methylenediurea, PS standards, and polydisperse PEG standards were used. They found that the effective number and weight-average molecular weights of the commercial UF resins lie between 250 and 500.

This article deals with solution properties of the products of the reaction between urea and formaldehyde in acid medium under the reaction conditions corresponding approximately to the conditions of the production of UF adhesives. Data on molecular weight distribution, parameters of polydispersity, and averages  $\bar{M}_n$ ,  $\bar{M}_w$ ,  $\bar{M}_z$  were obtained mainly by the method of analytical GPC together with vapor pressure osmometry, turbidimetry, precipitation fractionation, and preparative GPC.

## EXPERIMENTAL

### Chemicals

The chemicals used were as follows: solvents: tetrahydrofuran (Germel, GDR), "purum," unstabilized; dimethyl sulfoxide (Lachema, Czechoslovakia), "purum." For measurements of molecular weights by vapor pressure osmometry, THF was rectified in a nitrogen atmosphere at 3.3 kPa and 35–87°C and dried over a molecular sieve Nalsit 3 Å; the urea was granulated (Duslo, Czechoslovakia) and crystallized in methyl alcohol, with a melting point of 132.8°C; formaldehyde: 37% water solution (Chemko, Czechoslovakia); dimethylol urea with a melting point of 126°C, prepared by methylation of urea and formaldehyde according to refs. 1, 6, 7; molecular sieves: Nalsit 3 Å and Nalsit 4 Å (sodium aluminosilicate), products of CHZJD, Czechoslovakia.

### Procedures

#### *Preparation of Standards of UF Resins*

Urea, dimethylol urea, and fractions of UF resin were used for calibration of GPC of UF resins.

Fraction Nos. 3 and 4 on the calibration GPC curve (Fig. 1) were prepared by

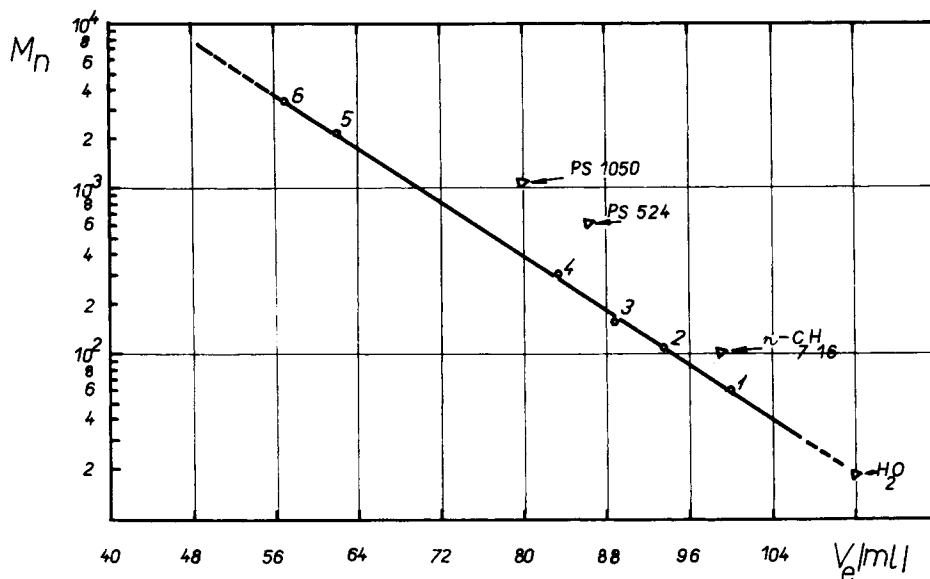


Fig. 1. Calibration dependence of GPC of UF resins. Columns: 120 cm Porasil A, 120 cm Porasil B, 60 cm Sephadex LH-20. Solvent: DMSO. (1) Urea; (2) dimethylol urea; (3) fraction of commercial UF resin prepared by the preparative GPC in THF with 10% water,  $\bar{M}_{n1} = 156^{(a)}$ ,  $\bar{M}_{n2} = 150^{(b)}$ ,  $R = 1.30^{(c)}$ , (4) fraction of commercial UF resin prepared by GPC in THF with 10% water;  $\bar{M}_{n1} = 302^{(a)}$ ,  $\bar{M}_{n2} = 308^{(b)}$ ,  $R = 1.30^{(c)}$ ; (5) fraction of commercial UF resin Umakol C (VCHZ, Czechoslovakia) prepared by repeated fractional precipitation:  $\bar{M}_n = 2030^{(a)}$ ,  $R = 1.34^{(c)}$ ; (6) fraction of commercial UF resin Umakol C (VCHZ, Czechoslovakia) prepared by repeated fractional precipitation:  $M_n = 3400^{(a)}$ ,  $R = 1.3^{(c)}$ ; where (a) VPO in DMSO,  $t = 80^\circ\text{C}$ ; (b) VPO in DMSO,  $t = 45^\circ\text{C}$ ; (c) checked by GPC using this calibration curve.

preparative GPC. The adhesive Umakol C (VCHZ Pardubice, Czechoslovakia) was fractionated. THF with 10% water was used as the solvent. Samples were injected into an injection valve using a syringe fitted with a filtration adapter. The solution (2 ml) with a concentration of 25 mg/ml was injected. Separation was carried out by employing a three-column system: Porasil A, 120 cm, Porasil B, 120 cm, Sephadex LH 20, 60 cm. The UF resin Umakol C was separated into six fractions. THF was evaporated from fractions on a vacuum rotary evaporator at  $25^\circ\text{C}$ . Water was removed from fractions by lyophilization.

Standard Nos. 5 and 6 (Fig. 1) were obtained by fractional precipitation of the UF resin Umakol C (VCHZ, Czechoslovakia). The precipitating system DMSO-acetone was chosen on the basis of turbidimetric studies of several systems. A resin solution (5%) in DMSO was prepared. For the first precipitation a mixed precipitant-acetone:DMSO (2:1) was employed. Ten fractions were obtained.

All fractions had wide distribution curves as was seen on the GPC chromatograms. The fractions were again dissolved in DMSO into solutions with the concentration of 20 g/liter. Before precipitation, acetone was added to the solution. Its amount was determined from a turbidimetric curve. The precipitation was carried out with a mixture of acetone and DMSO (2:1). Each fraction from the first precipitation separated into three fractions. The precipitate of the middle fraction was isolated by centrifugation on a preparative centrifuge with rotor cooling at the temperature of a centrifuged liquid of  $20^\circ\text{C}$  at 4000 rev/min.

The precipitation was repeated four times, the middle fraction of the three fractions obtained being used for each precipitation. Fractions were filtered by sucking off on a sintered glass filter, dried with a stream of nitrogen in flasks under stirring, and definitely dried in vacuum over  $P_2O_5$  at laboratory temperature. The quality of fractions was controlled by GPC using DMSO as the solvent and the system of columns described for the preparation of fractions 3 and 4.

Molecular weight determination was done employing equipment of VPO (Knauer, Germany); solvent: DMSO, thermistor: Universal. For establishing the calibration constant, urea (melting point  $132.5^\circ C$ ) was used (Fig. 2). The measurement was performed at 45 and  $80^\circ C$  on two pieces of apparatus.

Since the dried samples of UF resins are hygroscopic, samples were weighed so that on pouring into weighed 5 ml ground joint vessels they were again dried to constant weight over  $P_2O_5$  in vacuum at  $25^\circ C$ . After weighing, dry DMSO was added readily. The samples were dissolved in thoroughly closed vessels in a laboratory shaker for 12 hr. The weight of the vessels was again checked after dissolution.

### Gel Permeation Chromatography

The apparatus consisted of a heated glass reservoir of solvent equipped with a stirrer, a pump with filters, and a shock absorber with the maximum pressure of 7 MPa, injection valve, stainless steel columns 10 mm in diameter, differential flow refractometer R 403 (Waters), counter with a 4 ml syphon. An automatic fraction collector (Czechoslovak Acad. Sci., Prague) type 201 was employed for preparatory works. Figure 1 shows the calibration dependence together with the conditions for separation.

### Turbidimetric Titration

Turbidimetric curves were measured with a Spekol spectrophotometer (Zeiss, Jena, GDR) with an adapter for turbidimetric titration. All measurements were done at 530-nm wavelength and  $25^\circ C$ . The precipitant was added under continuous stirring in 30 min intervals and in 0.2-ml portions. The solvents used were water, DMSO, DMF, THF, and their mixtures with 5, 10, 20, and 40% water.

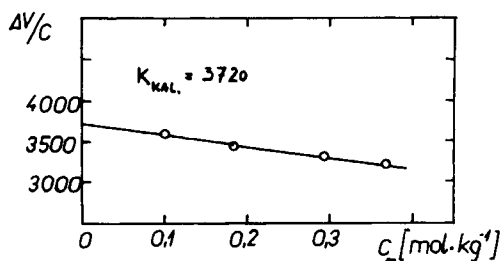


Fig. 2. Determination of the calibration constant for measuring molecular weights of UF resins by VPO. Standard: urea, solvent: DMSO,  $t = 80^\circ C$ .  $V$  is the deviation of the galvanometer of VPO apparatus proportional to the temperature difference between solution and solvent thermistor.  $C$  is the concentration (g/liter kg of solvent);  $C_m$  is the molal concentration of standard (mole/liter kg of solvent);  $M_n = (\lim_{C_m \rightarrow 0} \Delta V/C_m) / (\lim_{C_m \rightarrow 0} \Delta V/C)$ .

Acetone, ethyl methyl ketone, methanol, ethanol, propanol, isopropanol, butanol, cyclohexanone, and acetone mixtures with these alcohols in various ratios were used as the precipitants. DMSO–acetone was chosen as the most appropriate system of solvent and precipitant for UF resins.

#### *Polycondensation of Urea with Formaldehyde*

The polycondensation was carried out as follows: Grandulated urea and 37% formaldehyde were used. A solution of formaldehyde (536 g) was added to a condensation three-neck flask with a reflux condenser and a stirrer; pH was adjusted to  $7.2 \pm 0.1$ , the solution was heated under stirring to  $50^\circ\text{C}$ , and then urea (120 g) was added. After dissolution of urea, pH of the reaction mixture was reduced to 4.5–5.0, reaction temperature raised to  $90^\circ\text{C}$  was kept constant for 3 hr. The samples (20 ml) were withdrawn every 15 min, then neutralized using 0.1 N NaOH to pH = 7.1 and cooled to  $5^\circ\text{C}$ .

## RESULTS

Partial solubility of the samples of some UF resins, mainly commercial adhesives, renders it possible to perform the chromatographic analysis only of the soluble fractions. Consequently, exact comparison of various samples becomes difficult. Our aim was to find the most suitable solvent. The solubility of UF resins was studied in the following solvents: water, THF, and THF with 5, 10, and 20% water; DMSO and DMSO with 5, 10, and 20% water; DMF and DMF with 5, 10, and 20% water; dioxan with 10, 20, 30, 40, and 50% water; formic acid (85%); carbon chloride; chloroform; benzene; methanol; ethanol; *n*-propanol; isopropanol; and acetone. The ability of dissolving was evaluated according to the number of measured preparations dissolved without turbidity. The UF preparations used for solubility measurements were UF adhesives—Aerolite, Cascamite, Diakol S, Diakol M, Diakol F, Umakol C, laboratory prepared UF adhesive with  $\overline{M}_n = 340$ , and the fraction of the UF adhesive having  $\overline{M}_n = 2030$ .

The most appropriate solvents were shown to be DMSO and dioxan with 40 and 50% water. A considerable number of UF resins studied (Aerolite, Ciba; Umakol C, VCHZ Czechoslovakia; Diakol S, Chemko, Czechoslovakia) were successfully dissolved in the system of THF with 10% water that can be easily evaporated at low temperature in preparative works. On the other hand, in the solvent systems of DMF and water, as was used by Armonas,<sup>2</sup> in GPC of formaldehyde thermosetting resins, we failed to prepare clear solutions from UF resins employed over the concentration range between 1 and 10%.

Molecular weights and distribution curves of the UF resins investigated were determined as follows: VPO in DMSO was used for estimating the molecular weights of narrow fractions of UF resins prepared by the preparative GPC and by repeated precipitation respectively. On the basis of the molecular weights and elution volumes of the fractions, urea and dimethylol urea, the calibration dependence was plotted (Fig. 1). The analyzed samples were separated by GPC, elution diagrams were converted to distribution curves by the calibration plot (Fig. 1). The evaluation of GPC chromatograms was based on the assumption of the proportionality between the refractive index of the fraction and weight concentration.

The points corresponding to the low-molecular-weight standards of polystyrene are drawn on the calibration curve for comparison purposes (Fig. 1): PS 600 (Pressure Chem. Co., Pittsburgh, PA),  $\bar{M}_n = 524$  (VPO in benzene),  $\bar{M}_w/\bar{M}_n = 1.10$  and PS 900 (Pressure Chem. Co.),  $\bar{M}_n = 1050$  (VPO in benzene),  $\bar{M}_w/\bar{M}_n = 1.10$ . Evidently, PS molecules have greater elution volumes in dimethyl sulfoxide than the molecules of UF polycondensates with the same molecular weight.

Figure 3 shows the differential distribution curves of molecular weights of polycondensates taken during condensation of urea with formaldehyde in acidic medium at 90°C. The integral curves of the samples are given in Fig. 4.

The average molecular weights  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$  are shown on the differential distribution curve of the polycondensate taken after 30 min of the reaction at 90°C (Fig. 3). The position of the average molecular weights is also seen on the integral distribution curve of the polycondensate taken after 60 min of polycondensation at 90°C (Fig. 4).

$\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ , polydispersity coefficient  $R$ , and standard statistical deviations of number and weight distribution of molecular weights  $\sigma_n$ , and  $\sigma_w$ , and the Hoseman-Schramek index  $g$  (Figs. 3 and 4, Table I) were calculated as follows:

$$\bar{M}_n = \int_0^{\infty} MN(M) dM \quad (1)$$

$$\bar{M}_w = \int_0^{\infty} MW(M) dM \quad (2)$$

$$\bar{M}_z = \int_0^{\infty} M^2W(M) dM / \int_0^{\infty} MW(M) dM \quad (3)$$

$$\sigma_n = \left( \int_0^{\infty} (M - \bar{M}_n)^2 N(M) dM \right)^{1/2} = (\bar{M}_w \bar{M}_n - \bar{M}_n^2)^{1/2} \quad (4)$$

$$\sigma_w = (\bar{M}_z \bar{M}_w - \bar{M}_w^2)^{1/2} \quad (5)$$

$$R = \bar{M}_w / \bar{M}_n \quad (6)$$

$$g = \sigma_n / \bar{M}_w \quad (7)$$

Here  $N(M)$  is the number distribution density and  $W(M)$  is the weight distribution density, both being normalized, i.e.,

$$\int_0^{\infty} N(M) dM = 1 \quad \int_0^{\infty} W(M) dM = 1$$

Table I contains the average molecular weights and parameters of polydispersity calculated from distribution curves.

During polycondensation the viscosity of the reaction mixture increases with the increasing number-average molecular weight  $\bar{M}_n$ , weight-average molecular weight  $\bar{M}_w$ , and averages  $\bar{M}_z$  (Fig. 5). A rise in the time of polycondensation is accompanied by an increase of polydispersity of the reaction mixture (Fig. 6).

We were able to study the increase in the polydispersity of UF polycondensates in acid medium to the viscosity of the reaction mixture of  $\eta_{25^\circ\text{C}} = 120$  m Pa sec with a 44% dry substance. The number-average molecular weight of the resin obtained at this viscosity was  $\bar{M}_n = 424.5$  and the weight-average molecular weight  $\bar{M}_w = 1477.1$ .

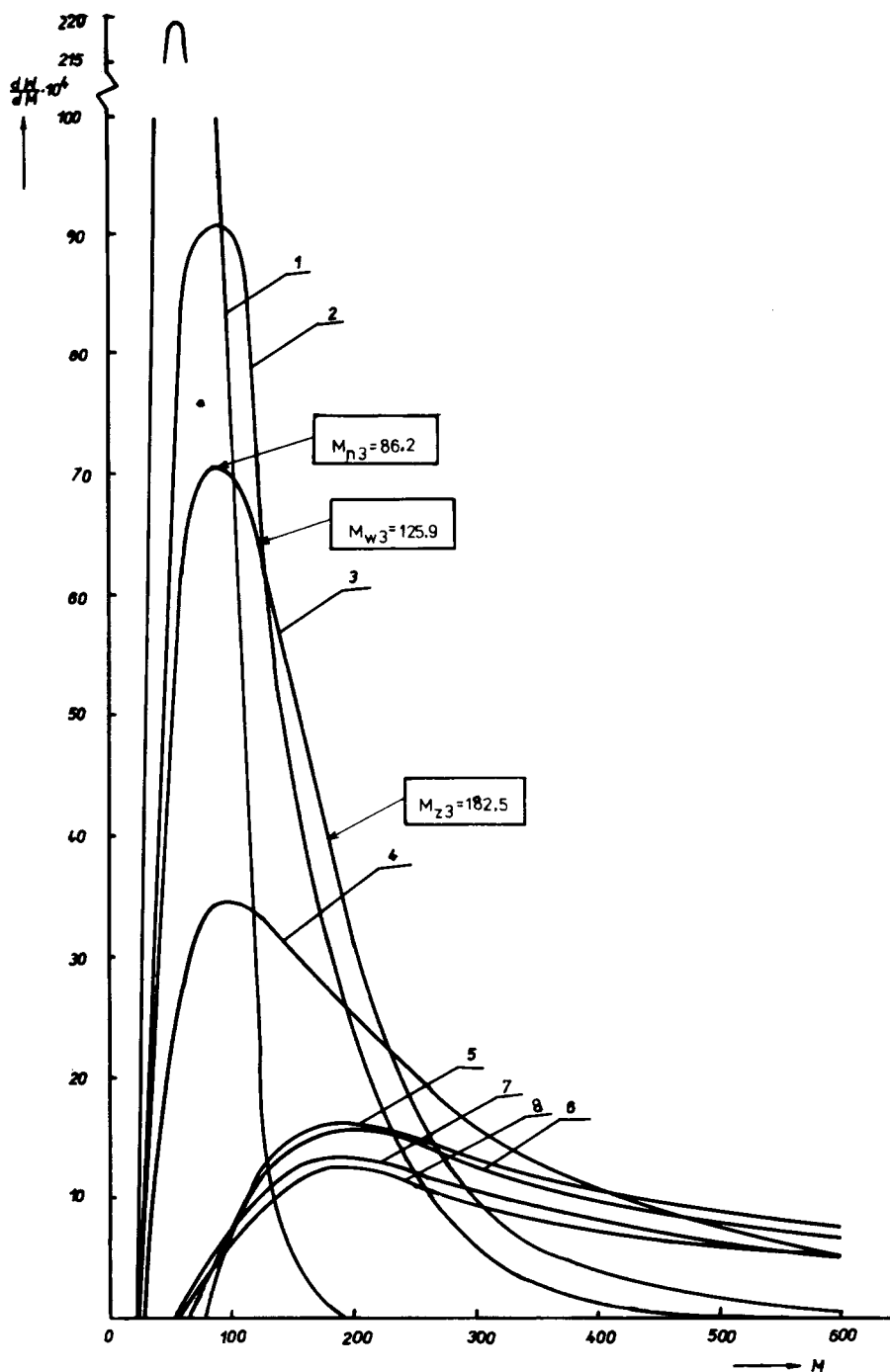


Fig. 3. Differential distribution curves for molecular weights of UF polycondensates after various time of polycondensation of urea with formaldehyde. Molar ratio formaldehyde/urea  $F/U = 2$ ,  $t = 90^\circ\text{C}$ , initial pH = 7.2. (1) Reaction time, 0 min. (The time was calculated from the moment of reaching  $t = 90^\circ\text{C}$ .) (2) 15; (3) 30; (4) 45; (5) 60; (7) 105; (8) 120 min.

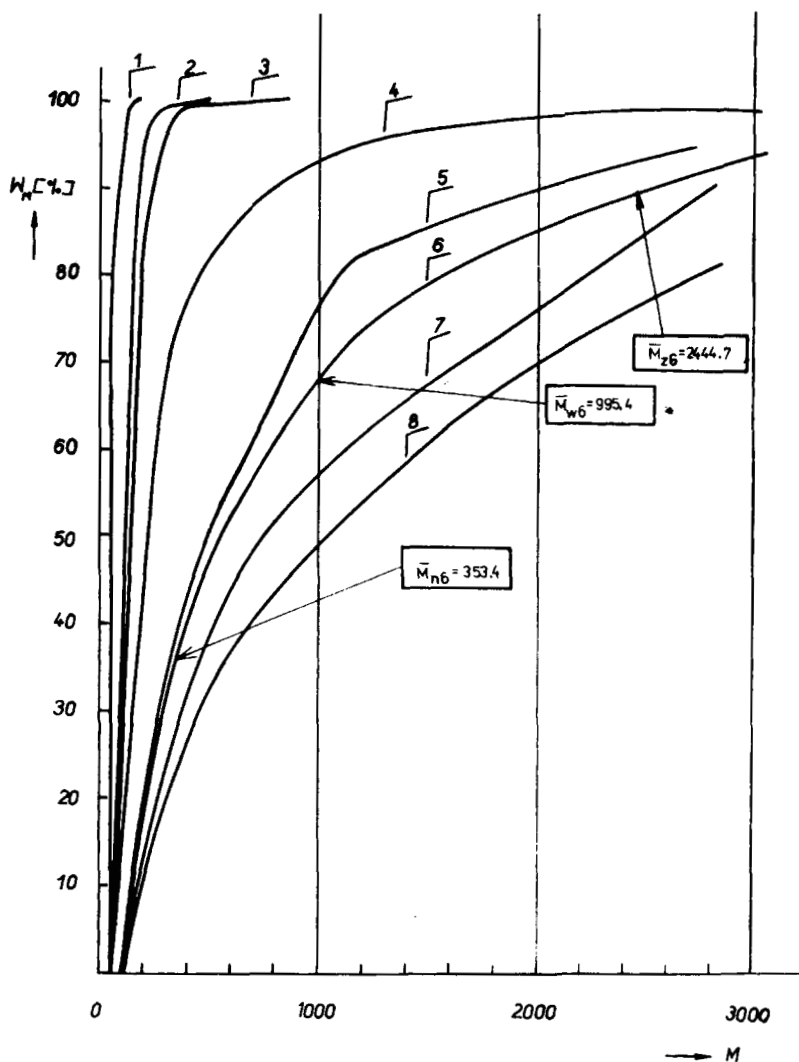


Fig. 4. Integral distribution curves of molecular weights of UF polycondensates after various time of the reaction between urea and formaldehyde. Conditions and denotation as in Fig. 3.

Kinetics of polycondensation were also followed in further stages up to the viscosity of the reaction mixture  $\eta_{25^\circ\text{C}} = 250$  m Pa sec. At viscosities higher than  $\eta_{25^\circ\text{C}} = 250$  m Pa sec, we failed to dissolve the polycondensate being formed in any solvent without turbidity. Above  $\bar{M}_n \approx 400$  and  $\bar{M}_w \approx 1400$ , only the composition of the soluble portion in DMSO can be studied by the methods described.

The investigation of the polydispersity of UF polycondensates was performed by the separation on the combined system of the GPC columns with inorganic incompressible gel Porasil (240 cm) and organic compressible gel Sephadex LH-20 (60 cm). The UF polymers were successfully separated in this way over the whole range of molecular weights studied. The advantage of the inorganic silica gel Porasil is its incompressibility; this is particularly desirable for separation rapid enough in solvents more viscous e.g. DMSO. It should be noted,



TABLE I  
Kinetics of Polycondensation of Urea with Formaldehyde; Apparent Solution Properties of the Reaction Products Obtained by GPC; Conditions for Polycondensation and Denotation of Samples as in Figure 3

No. <sup>a</sup>	Time of polycondensation (min) <sup>b</sup>	25°C <sup>d</sup> (m Pa sec)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	Molecular weight of highest fraction found by GPC ( $M_{max}$ )	R	g	$\sigma_N$	$\sigma_w$	Stage (Fig. 8)
1	0	1	46.4	553.2	61.2	$1.8 \times 10^2$	1.15	0.39	17.7	20.6	
2	15	2	74.9	102.6	141.2	$5.5 \times 10^2$	1.37	0.61	45.6	62.9	
3	30	5	86.2	125.9	182.5	$8.0 \times 10^2$	1.46	0.67	58.5	84.4	I
4	45	10	146.2	356.3	1067.0	$6 \times 10^3$	2.50	1.42	179.0	506.3	
5	60	14	339.3	825.4	1848.9	$8 \times 10^3$	2.44	1.11	406.1	919.1	II
6	75	29	353.4	995.4	24444.7	$1 \times 10^4$	2.82	1.21	476.3	1201.1	
7	105	60	404.3	1360.5	2927.8	$1.5 \times 10^4$	3.37	1.07	621.8	1460.2	
8	120	82	424.5	1477.1	2987.9	$2 \times 10^4$	3.48	1.01	668.4	2493.9	III
9 <sup>c</sup>	150	135	314.9	1700.2	6533.7	$(3-4) \times 10^4$	5.40	1.69	660.5	2866.7	

<sup>a</sup> The numbering of the samples is the same as in Figs. 3 and 4.

<sup>b</sup> Time of polycondensation was measured on the reaction mixture temperature of 90°C.

<sup>c</sup> The sample showed slight turbidity after dissolution in DMSO.

<sup>d</sup> Viscosity of the reaction mixture is in m Pa sec.

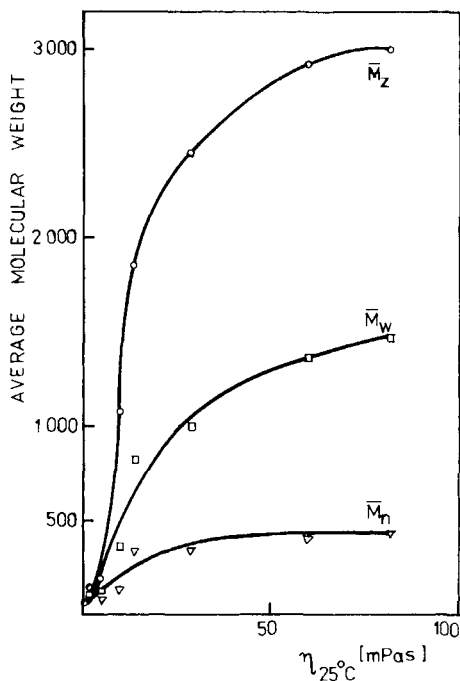


Fig. 5. Relation between average molecular weights  $\bar{M}_n$ ,  $\bar{M}_w$ ,  $\bar{M}_z$ , and viscosity of the reaction mixture  $\eta_{25^\circ\text{C}}$ .

however, that inorganic gels have relatively little effectiveness. They reduce the effectiveness of separation, in our case in mainly higher-molecular-weight fractions. Figure 4 shows relatively slight changes in distribution curves after 1 hr of polycondensation. As is seen from Table I, the Hoseman-Schramek index  $g = \sigma_w \bar{M}_w$  expressing distribution in the region of higher molecular weights of polycondensation significantly increases in the initial stage of the reaction (in contrast to the polydispersity parameter  $R = \bar{M}_z/\bar{M}_n$ ). In the higher stage,

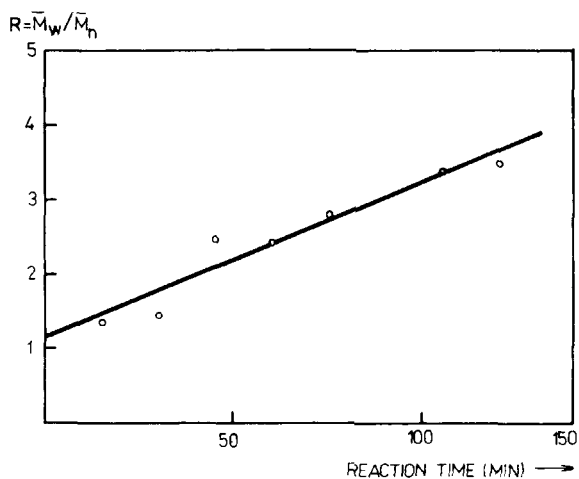


Fig. 6. Increase in the polydispersity coefficient during polycondensation of urea with formaldehyde.

relatively smaller changes in the composition of the high-molecular-weight fractions are camouflaged on the chosen GPC system by errors of measurements and sample preparation.

Statistical standard deviations of the number- and weight-average molecular weight distributions  $\sigma_n$  and  $\sigma_w$  increase successively in the initial methylol stage and in the stage of lower oligomer formation as well as in the formation of macromolecules with higher molecular weights. In the domain of the total polycondensate solubility in DMSO, the statistical deviation of the number-molecular-weight distribution of the polycondensate attained the value of  $\sigma_n = 6 \times 10^2$  and for the weight distribution  $\sigma_w = 2 \times 10^3$ .

## DISCUSSION

The initial stage of condensation of urea with formaldehyde, i.e., formation of methylolated urea derivatives and dimers, is well known. These components of the reaction mixture can be isolated as chemical individuals. For describing a further course of polycondensation, average parameters of the solution properties have to be used characterizing the reaction mixture in the given stage, such as the data on average molecular weights, polydispersity parameters, and differential and integral distribution curves.

The present article describes solution properties from the point of view of the GPC method and vapor pressure osmometry. For simplification, we do not use the term "effective" molecular weight, because obviously the methods studying solution properties, such as GPC and osmometry, are comparative procedures. The determined values, in particular those for hydrophilic thermosetting resins, depend on the measurement conditions, the solvent used, degrees of solvation and association, choice of standards, or, to a lesser extent, on temperature.<sup>4,5,8-10</sup>

The course increase of polycondensate molecules was investigated over the whole range of solubility of the reaction mixture in DMSO. Polycondensation was performed in an acid medium (pH = 4.5-5) at a molar ratio between formaldehyde and urea 2:1 by adding urea to a water formaldehyde solution at 50 and then at 90°C for 3 hr. GPC, VPO, fractional precipitation, turbidimetric titration, and viscometry were used.

Polycondensation of urea with formaldehyde is formally considered to take place in three stages, though the properties of the reaction mixture do not change suddenly and individual stages do not differ very much from each other.

### **First Stage: Formation of Methylolated Urea Derivatives and Low Oligomers—Dimers and Trimers**

Under the chosen reaction conditions, the first stage takes 30-45 min. The viscosity of the reaction mixture has at 25°C the value of 5-10 m Pa sec. The number-average molecular weight increases to approximately  $\bar{M}_n = 100$  and the weight-average molecular weight to about  $\bar{M}_w = 200$ . More than 95% of the molecules have the molecular weight  $M < 200$ . A small amount of a higher-molecular-weight product is formed, which, however, does not significantly affect the polydispersity of the polycondensate. The content of the higher-molecular-weight fractions reaches 1 wt %, the molecular weight of the largest molecules

found in this stage being  $850 \pm 50$ . The UF resins obtained show narrow molecular weight distribution: the polydispersity coefficient is  $R < 1.5$ . Statistical standard deviations  $\sigma_n$  and  $\sigma_w$  are smaller than 100 molecular weight units.

### **Second Stage: Formation of Soluble Portions with the Maximum Effective Molecular Weight between $10^3$ and $10^4$**

The portion of the low-molecular-weight oligomers with  $M < 200$  decreases. Commercial UF adhesives are usually produced in the second stage. Viscosity of the reaction mixture at  $25^\circ\text{C}$  ranges between 5 and 100 m Pa sec. The average molecular weights of the polycondensates formed are  $\bar{M}_n \leq 500$ ,  $\bar{M}_w \leq 1500$ . The polydispersity coefficient  $R$  is  $1.4 \div 3.5$ .

### **Low-Molecular-Weight Products**

Methylol urea and the lowest oligomers are condensed to products with higher molecular weight. The content of molecules with  $M < 200$  gradually decreases to 10–20%. The polycondensates contain a considerable number of molecules with the molecular weight of the order of magnitude  $10^3$  (to 50%) and a certain amount of molecules having a molecular weight of  $10^4$ . In this stage, the presence of the molecules with a maximum molecular weight of  $2 \times 10^4$  was confirmed.

The polycondensates prepared in the second stage show a wide molecular weight distribution. The values of the Hoseman–Schramek index are greater than unity ( $g = \sigma_w/\bar{M}_w > 1$ ) and at  $\bar{M}_n \leq 450$  and  $\bar{M}_w \leq 1500$ , they attain statistical deviations of  $\sigma_n \leq 700$  and  $\sigma_w \leq 1500$ .

### **Third Stage: Beginning of the Formation of Fractions Insoluble in Any Solutions of UF Resins**

Solution properties can no longer be quantitatively studied. Fractions insoluble in DMSO start forming in the approximate viscosity range of  $\eta_{25^\circ\text{C}} = 80\text{--}100$  m Pa sec. The samples were withdrawn up to a viscosity of  $\eta_{25^\circ\text{C}} = 250$  m Pa sec. The molecular weight again increases and the degree of crosslinking increases to such an extent that the solubility of the molecules being formed begins to decrease markedly. In the soluble portion of the polycondensates the products with the increased molecular weight were identified to about  $(3\text{--}5) \times 10^4$ . The mentioned crosslinking reactions and the rise in molecular weight lead to a rapid increase in the viscosity of the reaction mixture (Fig. 7). A study of the solution properties of polycondensates is in this range complicated and in higher stages impossible.

The above-described division of the polycondensation reaction can be, besides its formal importance, also of practical significance: The first stage can be described almost completely by paper, thin layer, or liquid chromatography, while for complete characterization of the solution properties in the second stage, GPC is necessary. The second stage is characteristic of the production of most UF adhesives; and at last, most resins from the third stage cannot be thoroughly characterized by solution properties because of their partial solubility.

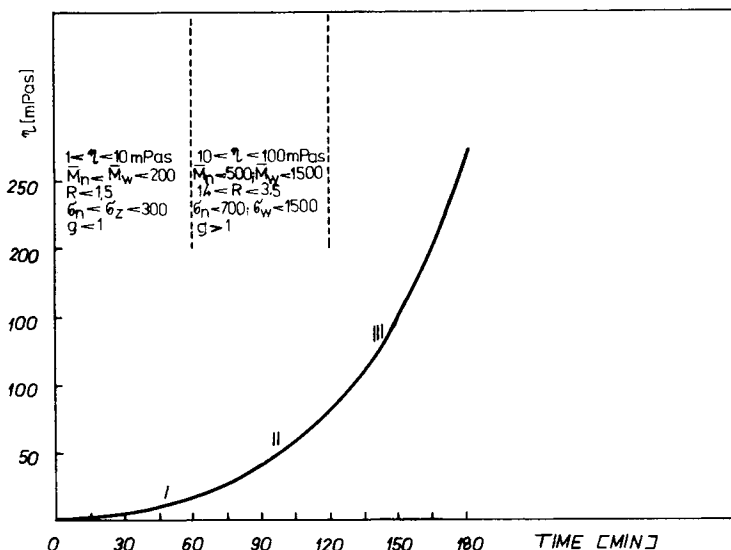


Fig. 7. Interpretation of the results of the study of kinetics of the polycondensation of urea with formaldehyde by GPC on the viscosity curve. Conditions as in Fig. 3. (I) Oligomers with  $M < 200$ ; (II) formation of the soluble reaction products in DMSO, with  $M$  between  $10^3$  and  $10^4$ ; (III) beginning of the formation of insoluble polycondensation products; complete determination of the solution properties is impossible in this and higher stages. Symbols:  $\eta_{25^\circ\text{C}}$  is the viscosity of the reaction mixture in m Pa sec;  $\bar{M}_n$  is the number-average molecular weight;  $\bar{M}_w$  is the weight-average molecular weight;  $\bar{M}_z$  is the average molecular weight determined by centrifugation calculated from distribution GPC plots according to eq. (5);  $R$  is the polydispersity coefficient;  $\sigma_n$  is the standard statistical deviation of number distribution; and  $\sigma_w$  is the standard statistical deviation of weight distribution.

## CONCLUSION

The polycondensation of urea with formaldehyde was studied over the whole region of the solubility of the reaction mixture. A reaction was chosen at the molar ratio between urea and formaldehyde 1:2 in an acidic medium (pH = 4.5–5) at  $90^\circ\text{C}$ .

The solution properties of the polycondensates obtained were investigated by GPC, VPO, turbidimetric titration, and fractional precipitation. The course of the polycondensation described was formally divided in the following stages (Fig. 7):

(1) Formation of methylolated urea derivatives and of the lowest oligomers. Solution properties: viscosity of the reaction mixture  $5 < \eta < 10$  m Pa sec;  $\bar{M}_n < 100$ ,  $\bar{M}_w < 200$ , polydispersity coefficient  $R < 1.5$ , statistical standard deviation of the number and weight distribution  $\sigma_n < \sigma_w < 100$  molecular weight units, and Hoseman-Schramek index  $g < 1$ .

(2) Decrease in the content of methylol urea and in the content of the lowest oligomers with  $M < 200$  and production of soluble molecules between  $10^3$  and  $10^4$ . The majority of industrial UF adhesives is produced in this stage. Solution properties:  $10 < \eta < 100$  m Pa sec,  $\bar{M}_n < 450$ ,  $\bar{M}_w < 1500$ ,  $1.4 < R < 3.5$ ,  $g > 1$ ,  $\sigma_n < 700$ ,  $\sigma_w < 1500$ .

(3) The study of the solution properties is very difficult and in higher stages impossible. Further, but limited increase in molecular weight of soluble macromolecules and the degree of crosslinking occurs, leading to the formation of insoluble products.

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