

# Wholly Aromatic Polyamide-Hydrazides

## I. A Viscometrical Method for Monitoring of Condensation Polymerization Reactions

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### Synopsis

A simple and practical viscometrical method for monitoring the progress of condensation polymerization reactions was investigated. It consisted of following the reaction mixture capillary flow time as a function of molar ratio of the reacting monomers in a polymerization reaction performed by gradual addition of terephthaloyl chloride (TCl) into solution of *p*-aminobenzhydrazide (ABH) in *N,N*-dimethylacetamide (DMA) solvent. The results obtained were compared to those from dilute solution viscometry and light scattering studies. This indicated that the observed increase in the reaction mixture capillary flow time accurately enough reflected the buildup of the molecular weight of growing polymer product during the course of this condensation polymerization reaction and that this viscometrical monitoring method provided an extremely practical tool for controlled preparation of the polymers of high and/or predetermined molecular weights by this synthetic route. A series of para-oriented, wholly aromatic amide-hydrazide polymers from ABH and TCl, was also characterized by viscometry and light scattering in DMA at 20°C, and the following viscosity-molecular weight relationship was determined:  $[\eta] = 5.16 \times 10^{-4} \bar{M}_w^{0.84}$ .

### INTRODUCTION

According to the accepted theory of step-growth polymerization reaction,<sup>1</sup> the weight average degree of polymerization,  $\bar{X}_w$ , is related to the molar ratio of the reacting functional groups, *r*, and to the extent of reaction, *p*, by the following equation:

$$\bar{X}_w = \frac{(1+p)(1+r)}{1+r-2rp} \quad (1)$$

However, since the average molecular weight of a polymer is simply given as the appropriate average degree of polymerization multiplied by molecular weight of a repeating unit,  $M_0$ , it follows from eq. (1) that the weight average molecular weight of a polymer product obtained by a condensation polymerization reaction is determined by the reaction conditions, in the manner described by the following equation:

$$\bar{M}_w = M_0 \cdot \frac{(1+p)(1+r)}{1+r-2rp} \quad (2)$$

These two equations imply that in order to prepare high molecular weight, linear polymer (with the weight average degree of polymerization of at least 100–200 which is usually required for useful polymer properties) by a condensation

polymerization reaction, very severe synthetic requirements, imposed by the nature of this step-growth process, must be precisely met.

First, even very small deviations of  $p$  and  $r$  from unity induce a rather dramatic decrease in the degree of polymerization,  $\bar{X}_w$ , and consequently also of the molecular weight of the polymer product. This is clearly illustrated by simple calculations from eq. 1, which yield that if  $p$  was exactly equal to 1.000,  $\bar{X}_w$  would decrease from 3998 to 398 if the stoichiometric imbalances were only 0.1 and 1 mol % (that is, if values of  $r$  were 0.999 and 0.99), respectively; or, if the equimolarity of the reacting functional groups was attained, that is, if  $r$  was equal to 1.000,  $\bar{X}_w$  would decrease from 1999 to 199 if  $p$  was reduced from 0.999 to 0.99. Secondly, in actual practice  $p$  may approach but never become equal to unity, so that, in accordance with the preceding, the experimental capability to adjust the molar ratio  $r$  to as close as possible to unity (that is,  $r \geq 0.98$ ) becomes of uppermost importance for successful preparation of a high molecular weight product by this synthetic route. That is why in condensation polymerizations it is necessary to use very pure monomers and to be able to control very precisely the molar ratio of the reacting functional groups during the course of their occurrence.\* Finally, any basic reaction to be used in a condensation polymerization must be fast and quantitative, and the conditions must be chosen so as to inhibit, to as high as possible extent, any potential side reactions in which one or both reacting monomers might be partially used up, unbalancing their molar ratio in a reaction mixture.

The practical implications of these requirements are very important from a viewpoint of a synthetic polymer chemist, and they could be summarized in the following way: no condensation polymerization reaction could possibly produce a high molecular weight polymer unless either both  $r$  and  $p$  are adjusted to at least 0.99 (when  $\bar{X}_w$  exceeds the value of 132), or, if any one of those experimental variables could be made equal to unity, the other must be brought to, or above, the value of at least 0.98 (when  $\bar{X}_w = 198$  if  $p = 1.00$  and  $r = 0.98$ ; or  $\bar{X}_w = 99$  if  $r = 1.00$  and  $p = 0.98$ ).

A very attractive approach by which the preceding requirements could be met is based on the utilization of some practical method for close monitoring of the increase of the molecular weight of a growing polymer product, or some other related property of polymerization system, during the course of condensation polymerization reaction. The reaction itself is then performed by gradual addition of one monomer into the other, so that the molar ratio of their reactive functional groups is gradually increased from zero to unity, under the conditions which are to be chosen so as to force it, as closely as possible, to completion. The main purpose of this, of course, is to determine that particular point at the end of experimental polymerization, at which the highest molecular weight product is formed, and at which the reaction is finished, but, more generally speaking, a reliable monitoring method should also enable one to correctly estimate the size of the growing polymer molecules at any stage during the course of the process and to allow, if that is desired, isolation of the products with predeter-

\* In the discussion of the effect of synthetic parameters on the degree of polymerization in step-growth polymerization reactions presented herein, the weight average degree of polymerization  $\bar{X}_w$  was chosen instead of the usually used number average degree of polymerization  $\bar{X}_n$ , because  $\bar{X}_w$  more closely corresponds to the viscosity measurements described later in this paper. For similar discussions in terms of  $\bar{X}_n$ , the reader is referred to Refs. 2-4.

mined lower molecular weights. If in such systems, the reaction conditions were adjusted so that acceptable high conversions were allowed, procedures could be improved to the level at which high molecular weight products could be routinely prepared.

Several monitoring methods have recently been described in the literature. These included: the use of  $^1\text{H}$  NMR to follow the disappearance of the growing polymer end groups<sup>5</sup> (as their concentration decreased with increasing chain length); the use of  $^1\text{H}$  NMR to follow the consumption of the monomer which was gradually added during the polymerization reaction into reaction mixture containing excessive amounts of the other<sup>6</sup> (if it could be detected as unreacted once in excess after the achievement of equimolarity); the use of dilute solution viscometry to determine and follow the increase of the inherent viscosity of the polymer samples which were periodically taken out of the reaction mixture during the course of polymerization reaction<sup>7</sup>; and the use of GPC to follow directly the increase of the molecular weight of the growing polymer product.<sup>6</sup>

These attempts proved to be very successful in helping to prepare high molecular weight products and initiated further interest in search of other simple and practical monitoring techniques. This paper describes the results obtained during the investigation of yet another such technique based upon simple control of the increase in relative viscosity of a homogeneous reaction mixture during the progress of a condensation polymerization reaction. It utilized usual measurements of the time required for a constant volume of reaction mixture to flow through a vertical glass capillary attached directly to the reaction flask, and was applied, to the condensation polymerization of *p*-aminobenzhydrazide (ABH) and terephthaloyl chloride (TCl) in *N,N*-dimethylacetamide (DMA) as solvent. This reaction was chosen for investigations because the experimental conditions could be adjusted so that both reactants and products remained soluble throughout the entire course of polymerization and because high conversions could be allowed.

## EXPERIMENTAL

### Materials

***p*-Aminobenzhydrazide (ABH).** Commercially available product (Cambrian Chemicals, England) was recrystallized from boiling ethanol, and its purity was determined by elemental analysis,  $^1\text{H}$  NMR spectroscopy, and melting point.  $^1\text{H}$  NMR in  $\text{DMSO}-d_6$ ,  $\delta$ :  $-\text{NH}_2$ , 5.59 ppm (s);  $=\text{N}-\text{NH}_2$ , 4.43 ppm (s);  $-\text{CON}-\text{H}$ , 10.12 ppm (s); aromatic, 6.67 ppm (d) ( $J$ , 8 cps) and 7.70 ppm (d) ( $J$ , 8 cps); mp, 220–221°C.

ELEMENTAL ANAL. Calcd for  $\text{C}_7\text{H}_9\text{N}_3\text{O}$ : C, 55.63%; H, 5.96%; N, 27.81%. Found: C, 55.28%; H, 5.92%; N, 25.08%.

**Terephthaloyl chloride (TCl).** Commercially available product (Fluka, Switzerland) was recrystallized prior to use from *n*-hexane which had previously been dried and distilled from  $\text{CaH}_2$ .  $^1\text{H}$  NMR in acetone- $d_6$ ,  $\delta$ : 7.60 ppm (s); mp, 82–83°C.

ELEMENTAL ANAL. Calcd for  $\text{C}_8\text{H}_4\text{O}_2\text{Cl}_2$ : C, 47.29%; H, 1.97%; Cl, 34.97%. Found: C, 48.05%; H, 2.11%; Cl, 35.30%.

***N,N*-dimethylacetamide (DMA).** Technical grade solvent was dried for 48 h over  $\text{BaO}$ , followed by 2-h reflux and distillation under reduced pressure.

The fraction which boiled at 58–59°C/11 mm Hg was collected and stored over molecular sieves before use.

### Methods

**Polymerization procedure.** A 250-mL four-necked, round-bottomed flask was equipped with a mechanical stirrer, thermometer, and a capillary glass viscometer. The neck to which a viscometer was connected was positioned just above the level of stirred reaction mixture in order to allow easy access to the solution for the flow time measurements. The apparatus was placed in a crushed-ice–water bath and cooled to between 0°C and 4°C. 3.78 g (25.03 mmol) of ABH was charged into the reaction flask followed by 100 mL of DMA. Stirring was started, and ABH was allowed to dissolve. When this was completed, 2.53 g (12.46 mmol) of solid TCl was slowly added, with constant stirring, during 60 min. After this addition total volume of the reaction mixture increased to 106 mL and the molar ratio of the two monomers,  $r$ , was established at 0.498. The reaction mixture was stirred for another 15 min before the first flow time determination. For this, a viscometer made of 86 mm long glass capillary with a 1.0 mm inner diameter was used. The reaction mixture was allowed to warm up to 25°C, and the apparatus was tilted so as to allow the desired aliquot of the solution to be pulled into viscometer applying a vacuum from a vacuum pump to its upper opening. The vacuum was then disconnected, and the time required for the reaction mixture to flow between the two permanent marks engraved on the viscometer walls was measured. This was repeated several times until at least two measurements agreed within 1%. At this stage of polymerization ( $r = 0.498$ ) a flow time of 13.4 s was thus obtained.

After this was completed, precisely 5.0 mL of the reaction mixture was sampled out for further characterizations, so that 23.85 mmol of ABH and 11.88 mmol of TCl in 101 mL of the total volume were left in the reaction flask. The system was cooled back to 0–4°C and another 0.49 g (2.42 mmol) of TCl was added during the next 10 min. This increased the molar ratio to 0.599 in 101.8 mL of the reaction mixture. 15 min later, the flow time determination was repeated in the described manner, and sample no. 2 was taken. This procedure was carried out analogously until the end of the reaction, so that 14 different samples, ranging from  $r = 0.498$  to  $r = 1.071$ , were obtained.

**Intrinsic viscosity.** Intrinsic viscosities were determined for all of the collected samples in DMA at  $20 \pm 0.5^\circ\text{C}$ . Solutions were prepared at room temperature in all cases. Their concentrations ranged from 0.49 to 0.52 g/dL. Flow times were determined at five different concentrations using Cannon viscometers which were selected to give solvent flow times in excess of 100 s. All flow times encountered were sufficiently long to justify neglect of kinetic energy corrections, and the lack of shear-rate dependance was verified. Intrinsic viscosities were determined by the usual double extrapolation of  $\eta_{sp}/c$  and  $(\ln \eta_{rel})/c$  to zero concentration. The plots obtained were linear in all cases.

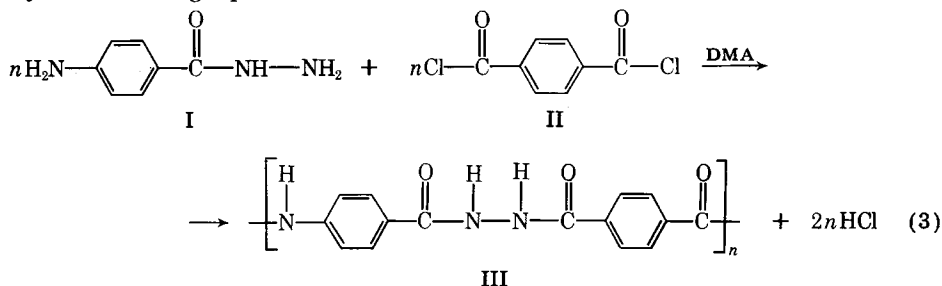
**Light scattering.** Light scattering data were obtained using a Brice Phoenix OM-2,000 Photometer. Measurements were performed in the angular range of 35° to 135° with blue light ( $\lambda = 436 \text{ \AA}$ ) at 20°C. The refractive index at 436 Å was measured at 20°C for five solutions using a Brice Phoenix Differential

Refractometer. The least-squares method resulted in  $dn/dc$  value of  $0.564 \text{ cm}^3/\text{g}$  with an estimated error of less than 5%.

## RESULTS AND DISCUSSION

### Condensation Polymerization Reaction

Condensation polymerization of *p*-aminobenzhydrazide, I, and terephthaloyl chloride, II, yields poly(terephthaloylimino-1,4-phenylhydrazide), III, as shown by the following equation:



The basic reaction employed here is the Schotten-Baumann condensation of an aromatic acid chloride and an amino-hydrazide, which is generally known to be fast and quantitative. This polymerization was first investigated by Frazer and Wallenberger<sup>8</sup> and later studied in more details by Preston and co-workers,<sup>9</sup> who showed that the rate by which hydrazide groups of ABH reacted with TCl was about seven times greater than that of the amino groups with the same acid chloride. This indicated that when this polymerization was performed by gradual addition of TCl into a solution of ABH monomer, the hydrazide groups of the latter reacted first, and the so-called "wholly ordered" polymer with alternating amide and hydrazide linkages was formed. The evolution of HCl by-product may be expected to show a twofold effect on this reaction. First, HCl acts as a reaction catalyst, and second, since it was shown to readily form complexes with DMA solvent,<sup>10</sup> this complexation should shift the polymerization equilibrium towards completion, and thus become an additional driving force for the process. Consequently, since the basic reaction is known as rapid even at low temperatures, and, since one of the polymerization products is continuously being withdrawn from the equilibrium, this condensation polymerization reaction is expected to proceed to acceptably high conversions and thus satisfy one of the mentioned requirements for preparation of high molecular weight products imposed by the nature of this step-growth process.

### Monitoring Method

Viscosity of a polymer solution at constant temperature and pressure has long been known to depend upon the polymer's molecular weight. This dependence has been the subject of large number of investigations which resulted in several postulated theories and a vast amount of collected experimental data. The results obtained led to better understanding of the relations existing between solution viscosity and the molecular weight of a polymer solute, and they eventually

offered quantitative bases for a variety of practical methods, which have ever since been widely used for determination of polymer molecular weights.

Having this in mind, it was attempted in this investigation to determine if one of these methods, the capillary viscometry, could be successfully applied to monitoring of the progress of condensation polymerization reactions by following the increase of the relative viscosity of a homogenous reaction mixture, if this property could reliably reflect the buildup of the molecular weight of a growing polymer, which occurs, during the course of reaction, as the molar ratio of the reacting functional groups is increased from zero to unity by gradual addition of one of the monomers into a stoichiometric excess of the other.

The monitoring method, because of the reasons stated at the beginning of this paper, need not necessarily offer the absolute value of the growing polymer molecular weight (for which it could always be additionally calibrated, of course), but only produce a measure of the relative increase of this property during the course of reaction, and sensitively show that point at which it ceases to increase further. Consequently, it was envisioned that following the change of the relative viscosity of a condensation polymerization reaction mixture, by measuring its capillary flow time, the purpose might be accomplished, and, since this technique is simple and practical, it was hoped to provide an easily accessible monitoring method which would not require any special or expensive instrumentation. In addition to this, such viscometrical method would also be fast and would not require, sometimes quite tedious and time-consuming, sampling of the reaction mixture, followed by isolation, washing, and drying of the polymer product, which are necessarily involved in the monitoring procedure performed by determination of the increase of inherent viscosity during the course of polymerization.

Capillary viscometry is based upon Poiseuille's law<sup>11</sup> which predicts that the viscosity of a solution,  $\eta$ , which flows through a capillary viscometer under its own head, is proportional to the volume flow time  $t$ , according to the following equation:

$$\eta = \frac{\pi \cdot R^4 \cdot g \cdot h \cdot d \cdot t}{8 \cdot V \cdot l} = K \cdot d \cdot t \quad (4)$$

where  $g$  is the gravitational constant,  $h$  is the effective hydrostatic head,  $V$  is the total volume of solution which flows through the capillary,  $d$  is the density of the solution,  $R$  and  $l$  are the radius and length of the capillary, and  $K$  is a constant which is the characteristic of the particular viscometer and which accounts for its geometrical shape.

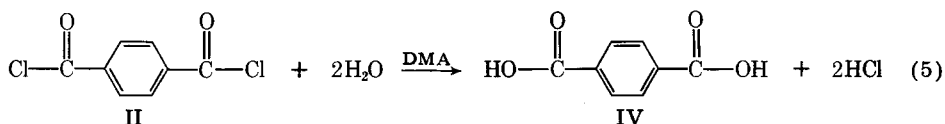
It follows from this equation that, for a particular capillary viscometer, the viscosity of a polymer solution is proportional to its density and to the volume flow time through that capillary, so that, since it is also known to be proportional to the solute's molecular weight, it was envisioned to examine in this work if the capillary flow time of a polymerization reaction mixture as the measure of its relative viscosity could also serve as a reliable indication of the relative increase of the growing polymer molecular weight, assuming that the change of the reaction mixture density during the course of reaction, would not significantly influence the results to jeopardize the main purpose.

However, there was still another effect to consider which was also expected to influence the reaction mixture flow time, and that was the change of reaction mixture concentration which occurred during the course of polymerization re-

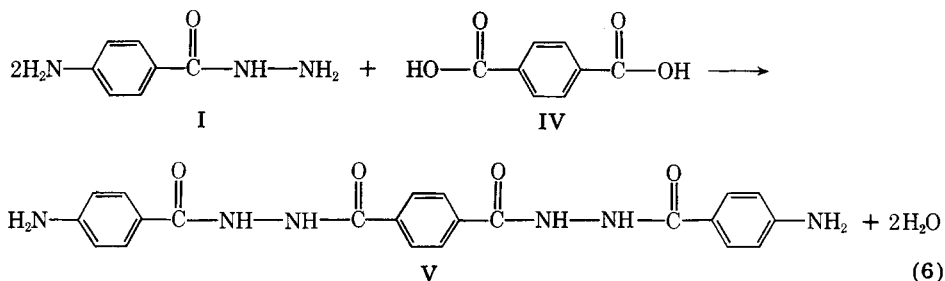
action due to the gradual addition of one of the reacting monomers into the solution of the other.<sup>12</sup>

In an attempt to estimate the magnitude by which this increase in polymerization reaction mixture concentration influenced the change of its capillary flow time, the following approach was undertaken. An experiment was performed in which the described polymerization reaction of *p*-aminobenzhydrazide and terephthaloyl chloride was simulated using the same monomers and DMA solvent which contained about 5% weight of added water as determined by measuring the ratio of the areas of two characteristic peaks corresponding to H<sub>2</sub>O and DMA in GC chromatograms obtained by utilizing "Porapak Q"-filled columns at 200°C. This water content was expected to be sufficient to assure that, under the experimental conditions used, all of the TCl monomer would be hydrolyzed into terephthalic acid upon its addition into the reaction mixture, so that while the acid thus formed would still be capable of reacting with hydrazide groups of ABH it would also fail to react with weakly basic aromatic amino groups left over after *r* reached the value of 0.5, and consequently would not allow any polymer formation, as shown by the following equations:

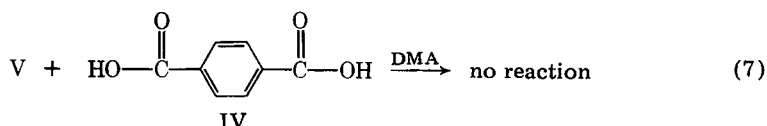
a. Hydrolysis of TCl monomer (at any value of *r*):



b. Reaction of terephthalic acid IV with hydrazide groups of ABH ( $0 < r < 0.5$ ):



c. Formation of ternary mixture ( $r > 0.5$ ):



It can be seen from these equations that once *r* exceeded the value of 0.5 in this system, the resulting solution could be considered as a simple ternary mixture composed of two different solute components (diamine, V, and terephthalic acid, IV) and DMA (or more precisely: DMA/HCl) solvent. In it, the amount of diamine [according to eqs. (6) and (7)] was kept constant, while that of terephthalic acid gradually increased following the increase of *r* due to continued addition of TCl, which was performed in the same manner as in polymerization

TABLE I  
Monitoring of the Condensation Polymerization Reaction of *p*-Aminobenzhydrazide (ABH) and Terephthaloyl Dichloride (TCl) by Capillary Viscometry<sup>a</sup>

Sample no.	<i>r</i>	Polymerization reaction mixture flow time <i>t</i> (s)	Concentration-dependent flow time <i>t<sub>c</sub></i> (s) <sup>b</sup>	Molecular-weight-dependent flow time ( $\Delta t$ ) (s)
1	0.498	13.4	12.4	1.0
2	0.599	14.0	13.0	1.0
3	0.697	15.0	13.9	1.1
4	0.748	24.2	22.4	1.8
5	0.798	40.8	37.8	3.0
6	0.848	79.2	48.4	30.8
7	0.898	142.2	55.1	87.1
8	0.945	300.0	80.5	218.9
9	0.948	314.6	81.1	233.5
10	0.983	658.4	95.3	563.1
11	0.997	1648.5	126.2	1522.3
12	1.027	1724.0	130.0	1594.0
13	1.056	1787.5	153.3	1634.2
14	1.071	1812.0	178.0	1634.0
15	1.120	1906.0	272.2	1633.8

<sup>a</sup> Volume flow times at 25°C through the vertical capillary glass viscometer ( $R = 1.00$  mm;  $l = 86.05$  mm).

<sup>b</sup> As determined in the experiment with ternary model-mixture.

reaction itself. This mixture represented then a model of the polymerization reaction mixture (in terms of composition) in which no polymerization reaction was taking place. Thus, the increase of its viscosity with increasing *r* (determined under the same experimental conditions as those applied to the polymerization reaction: temperature, apparatus, order of addition, and amounts of the components added) was expected to closely simulate the contribution of increasing concentration to the overall viscosity of the investigated polymerization reaction mixture, which would have been observed if it were possible to separate this contribution from that of the growing polymer molecular weight.\* Based upon such hypothesis, and since at any particular value of *r* larger than 0.5 the viscosity of this model mixture (expressed by its corresponding capillary flow time *t<sub>c</sub>*) was dependent only on its concentration (see the Appendix), experimentally determined *t<sub>c</sub>* values were taken as representing the concentration contribution to the overall viscosity of polymerization reaction mixture (expressed accordingly by its corresponding capillary flow time *t*). The difference between these two values:  $\Delta t = t - t_c$  was then accepted as representing a quantity which reflected the desired contribution of the growing polymer molecular weight to the overall

\* There is, of course, a certain small difference,  $\Delta c$ , existing, at any particular value of *r* larger than 0.5, between the actual concentration of the ternary mixture,  $c_{tm}$ , and that of the polymerization reaction mixture  $c_{pm}$ . This difference is due to the difference in molecular weights of terephthalic acid and *p*-OC—C<sub>6</sub>H<sub>4</sub>—CO— group which enter into the compositions of solute fractions of these two mixtures. Because of this, and since  $\Delta c = c_{tm} - c_{pm} > 0$ , it should be kept in mind that experimentally determined *t<sub>c</sub>* values were somewhat larger, while at the same time corresponding  $\Delta t$  values were smaller, than what they would have been if the concentrations  $c_{tm}$  and  $c_{pm}$  were exactly the same. However, although this could be appropriately taken into account, neglect of such correction may only influence to a certain extent, the sensitivity of the monitoring method but not jeopardize its main purpose.



viscosity of polymerization reaction mixture. Consequently, as such,  $\Delta t$  was further used as a perhaps more realistic monitoring parameter than the uncorrected  $t$  value itself.

The results obtained by applying this approach to the investigated polymerization reaction are shown in Table I and Figure 1.

It can be seen from this figure that the S type curves were obtained by plotting polymerization reaction mixture capillary flow time  $t$  as well as its concentration corrected value  $\Delta t$  against the molar ratio of TCl and ABH,  $r$ . Both flow times remained practically constant throughout the major part of the reaction (until  $r$  reached the value of about 0.8), when they started to increase, first slowly and then much more rapidly (between the  $r$  values of 0.948 and 0.997), after which they slowed down and finally leveled off at  $r = 1.056$ . Assuming that  $\Delta t$  reliably reflected the growing polymer molecular weight, this can be taken as in accordance with the theoretical understanding of the condensation polymerization reaction, which predicts the major buildup of the latter only above the molar ratio of the reacting monomers of 0.95.

Furthermore, when the end point of the polymerization reaction was reached, as the last of the excessive amino functional groups were used up, all of the polymer end groups would turn from amino into acid chloride, as shown by eq. (8), and any further quantity of TCl monomer added into the system after that point would be expected to remain unreacted, inducing no further change in the molecular weight of the polymer product and thus no further increase in the concentration corrected polymer mixture flow time, just as observed here for

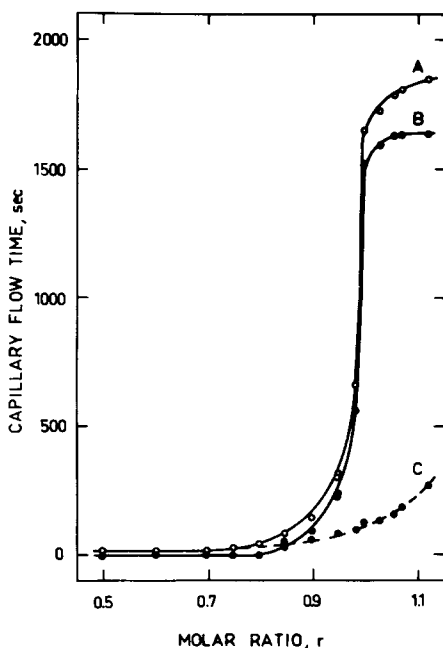
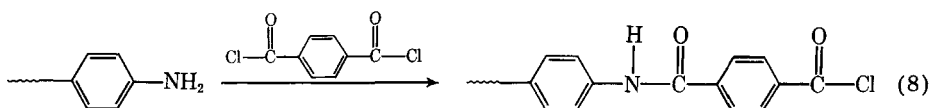


Fig. 1. Monitoring of the condensation polymerization reaction by reaction mixture capillary flow time determination: (A) (O) uncorrected polymerization reaction mixture flow times  $t$ ; (B) (●) molecular-weight-dependent (i.e., concentration corrected) flow times,  $\Delta t$ ; (C) (○) concentration-dependent flow times  $t_c$  (as determined in the experiment with ternary model-mixture).

&gt; 1.056:



The deviation from ideality (the end point above  $r = 1.000$ ), can be ascribed to the consumption of TCl monomer in some side reaction, for example, hydrolysis of the acid chloride into terephthalic acid if even the traces of moisture were present in the polymerization medium, which would be expected to occur rather than in polymerization reaction itself.

### Dilute Solution Viscometry

In order to examine how well did the change in the concentration-corrected reaction mixture capillary flow time  $\Delta t$  really reflect the change in the growing polymer molecular weight during the course of polymerization reaction, the intrinsic viscosities were determined for the samples periodically taken from the polymerization reaction mixture at selected values of  $r$ . The results obtained are shown in Table II and compared with corresponding  $\Delta t$  vs.  $r$  function in Figure 2.

It can be seen from this figure that the general shape of  $[\eta]$  vs.  $r$  was quite similar to that of  $\Delta t$  vs.  $r$  of Figure 1, and that the S-type curve was obtained again. Comparing the two curves more closely, it follows that intrinsic viscosity reached its maximum, and ceased to increase further, at about the same  $r$  value at which the concentration-corrected reaction mixture flow time did, indicating that leveling off of  $\Delta t$  vs.  $r$  accurately depicted the polymerization reaction end point at which the maximum molecular weight of the growing polymer was at-

TABLE II  
Dilute Solution Viscometry and Light Scattering Data for the Growing Polymer Product during the Course of the Condensation Polymerization Reaction of *p*-Aminobenzhydrazone (ABH) and Terephthaloyl Dichloride (TCl)

Sample no.	$r$	$[\eta]$ (dL/g) <sup>a</sup>	$\bar{M}_w$ <sup>b</sup>	$\bar{M}_{w(\text{calcd})}$ <sup>c</sup>
1	0.498	0.255	1610	1680
2	0.599	0.307	2010	2240
3	0.697	0.389	2660	3150
4	0.748	0.514	3710	3900
5	0.798	0.578	4260	5000
6	0.848	0.735	5670	6830
7	0.898	1.096	9130	10,460
8	0.945	1.514	13,410	19,870
9	0.948	1.731	15,730	21,050
10	0.983	2.034	19,060	65,560
11	0.997	2.095	19,740	374,100
12	1.027	2.155	20,420	—
13	1.056	2.180	20,700	—
14	1.071	2.191	20,830	—

<sup>a</sup> In DMA at  $20 \pm 0.5^\circ\text{C}$ .

<sup>b</sup> Calculated on the bases of the intrinsic viscosity data.

<sup>c</sup> Calculated from eq. (2) using  $p = 1$  and  $M_0 = 281$ .

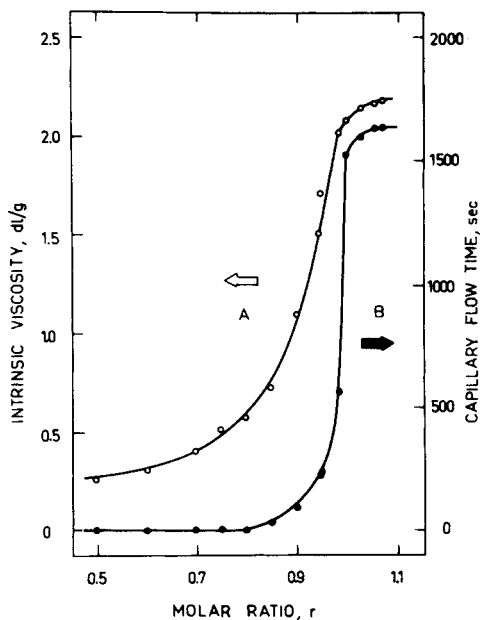


Fig. 2. Comparison of the polymer molecular weight increase as determined by intrinsic viscosity determinations (A) and concentration-corrected reaction mixture capillary flow time measurements (B).

tained. It can also be seen that the increase in  $\Delta t$  was somewhat steeper than that of  $[\eta]$ , as well as that  $[\eta]$  started to increase earlier in the reaction (that is, at lower values of  $r$ ) for the reasons which could not be explained on the basis of these data only. Because of this, it was decided to determine actual molecular weights of the obtained polymer samples and to compare them with the values theoretically predicted by eq. (2).

### Molecular Weight Determinations

Weight-average molecular weights of the products isolated from reaction mixture samples 7, 8, 13, and 14 of Table I were determined by light scattering, and the data obtained are listed in Table III and plotted as  $\log [\eta]$  against  $\log \bar{M}_w$  in Figure 3. The resulting straight line could best be described (using the least-squares method) by the following viscosity-molecular weight relation:

$$[\eta] = 5.15 \times 10^{-4} \bar{M}_w^{0.84} \quad (9)$$

TABLE III  
Molecular Weight and Viscosity Data for Poly(terephthaloylimino-1,4-phenylhydrazide) in DMA at 20°C

Sample no.	$[\eta]$ (dL/g)	$\bar{M}_w$
7	1.096	9500
8	1.514	13,700
13	2.180	19,200
14	2.191	23,000

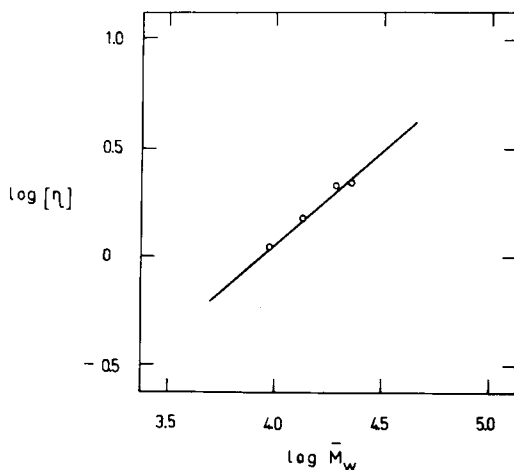


Fig. 3. Molecular weight dependence of intrinsic viscosity of poly(terephthaloylimino-1,4-phenylhydrazide) in DMA at 20°C.

The values obtained here for the constants in the equation above, for this polyamide-hydrazide in the solution of DMA at 20°C, with the polymer molecular weights ranging from 9500 to 23,000, should be compared with those reported for the same polymer in DMSO at 25°C, which were:  $6.15 \times 10^{-5}$  and 1.06, originally by Burke<sup>13</sup>;  $2.90 \times 10^{-4}$  and 0.91, later by Bianchi and co-workers<sup>14</sup>; and finally  $1.05 \times 10^{-3}$  and 0.795 by the same group of authors.<sup>15</sup> The molecular weight exponent found here is noticeably larger than those usually found for highly coiling macromolecules in good solvents, but it is also somewhat smaller than the previously mentioned values of 1.06 or 0.91. It should also be noted that this wholly aromatic polyamide-hydrazide shows much higher intrinsic viscosities than most random coiling polymers of the comparable molecular weights, as reflected in the relatively high value of the molecular weight exponent of eq. (9). This is probably due to its all-para orientation which is expected to induce very much restricted chain flexibility, because of which macromolecular chains of poly(terephthaloylimino-1,4-phenylhydrazide) should assume a highly extended conformation in solution in comparison with most randomly coiling synthetic polymers.

Finally, using eq. (9), molecular weights were calculated for all samples of Table I, and the values thus obtained are plotted against  $r$  and compared in Figure 4 to those theoretically predicted for  $\bar{M}_w$  by eq. (2), assuming that  $p = 1$  and that  $\bar{M}_w/\bar{M}_n = 2$ .\*

It can be seen from this figure that the experimentally obtained  $\bar{M}_w - r$  curve lies between the calculated  $\bar{M}_w - r$  and  $\bar{M}_n - r$  curves, but more to the side of the former. It can also be seen that experimentally obtained values of  $\bar{M}_w$  are somewhat smaller than those theoretically calculated, which may very well be due to the actual value of  $p$  being very close but not exactly equal to unity as assumed herein.

\* It should, of course, be kept in mind that these assumptions:  $p = 1$  and  $\bar{M}_w/\bar{M}_n = 2$  are precisely correct only towards the end of polymerization reaction, i.e., when the average molecular weights are high. For that reason, the comparison of experimentally obtained and theoretically predicted molecular weights shown in Figure 4 should be taken approximatively at lower values of  $r$ .

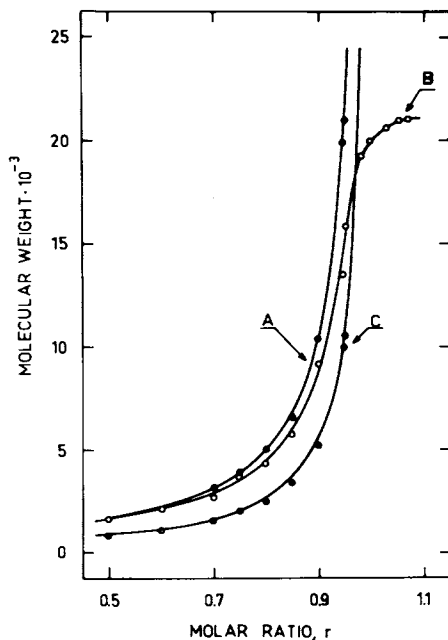


Fig. 4. Comparison of the calculated [(A)  $\overline{M}_w$ ; (C)  $\overline{M}_n$ ] and experimentally determined (B) polymer molecular weight increase during the condensation polymerization reaction of ABH and TCl. For calculation of (A) and (C),  $p = 1$  was assumed.

### Conclusions

Based upon the experimental results obtained, it has been shown in this work that the viscometrical method described herein reflects accurately enough the increase of the growing polymer molecular weight during the course of a condensation polymerization reaction performed by gradual addition of one monomer into the other. In spite of the fact that the concentration of the reaction mixture changed throughout the process, the increase of the polymerization reaction mixture flow time appears to be largely dominated by the change in the growing polymer molecular weight, and, consequently, the method seems to be applicable to monitoring purposes. According to the results presented herein, it seems clear that detection of the polymerization end point is somewhat more precise when concentration-corrected capillary flow time  $\Delta t$  is followed as a monitored parameter, although in usual laboratory practice the purpose will be accomplished even without application of this correction, i.e., by simple and direct monitoring of the uncorrected reaction mixture capillary flow time  $t$ . Finally, considering also that this method could easily be calibrated to reflect directly the actual increase of the molecular weight of the growing polymer (by some suitable method such as, for example, light scattering) in combination with its unusual simplicity, it provides a new and extremely practical tool for successful monitoring of condensation polymerization reactions which throughout their entire course take place in homogenous reaction mixtures, or in which growing polymer products remain soluble in liquid phase of a heterogenous system.

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## APPENDIX

Suppose that for a physical mixture such as the ternary mixture described herein, viscosity could be very generally taken, described by the well-known Huggins equation,<sup>12</sup> as follows:

$$\eta_m = \eta_0(1 + [\eta]c + K[\eta]^2c^2) \quad (10)$$

where  $\eta_m$  and  $\eta_0$  are the viscosities of mixture and solvent, respectively, and  $[\eta]$  and  $c$  represent the intrinsic viscosity and the mass concentration of the solute while  $K$  is the so-called Huggins coefficient, which is the constant characteristic of a given solvent-solute system. Following the approach of Peeters and Staverman,<sup>17</sup> we can further write

$$c = c_1 + c_2 \quad (11)$$

and

$$[\eta]c = [\eta]_1c_1 + [\eta]_2c_2 \quad (12)$$

where the subscripts 1 and 2 denote diamine V and terephthalic acid IV of eqs. (5) and 6, respectively. Substituting eq. (12) in eq. (10), the following expression for the viscosity of a ternary mixture is obtained:

$$\eta_m = \eta_0(1 + [\eta]_1c_1 + [\eta]_2c_2 + K_1[\eta]_1^2c_1^2 + 2K_{12}[\eta]_1[\eta]_2c_1c_2 + K_2[\eta]_2^2c_2^2) \quad (13)$$

Since above the  $r$  value of 0.5 in the experiment with model mixture described herein,  $[\eta]_1$  became and remained constant [in accordance with eqs. (6) and (7)], it can clearly be seen from the equation above that at constant temperature  $\eta_m$  was dependent on total solute concentration ( $c_1$  and  $c_2$ ) only. Consequently, the increase in viscosity detected in this experiment (curve C of Fig. 1) was due only to the increasing concentration of the mixture which occurred within the investigated range:  $0.5 < r < 1.12$ .

**Note Added after Submission of Manuscript:** Applying the described viscometrical monitoring method to the polymerization reaction investigated in this work, poly(terephthaloylimino-1,4-phenylhydrazide) having  $\bar{M}_w$  of 64,500 ( $[\eta] = 5.65$  dL/g in DMA at 20°C) was recently prepared in the author's laboratories. This molecular weight appears to be by about 15,000 higher than the highest value previously reported in the literature,<sup>16</sup> although, wherever syntheses were described, in the earlier works the same polymerization reaction was always performed in *inert* atmosphere, which, for the obvious chemical reasons, is much more favorable to preparation of high molecular weight products than the herein described open-to-air reaction system. Consequently, it seems that this information further emphasizes the capabilities inherent in this monitoring method for preparation of high molecular weight polymers by step-growth polymerization reactions.

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