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

Self-Reguiating Poiycondensations. II. A Study of the Order Present in Polyamide-Hydrazides Derived from Terephthaloyl Chloride and p-Aminobenzhydrazide

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To cite this Article Morrison, R. W. , Preston, J. , Randall, J. C. and Black, W. B.(1973) 'Self-Reguiating Poiycondensations. II. A Study of the Order Present in Polyamide-Hydrazides Derived from Terephthaloyl Chloride and p-Aminobenzhydrazide', Journal of Macromolecular Science, Part A, 7: 1, 99 — 118

To link to this Article: DOI: 10.1080/00222337308061133

URL: http://dx.doi.org/10.1080/00222337308061133

J. MACROMOL. SCI.—CHEM., A7(1), pp. 99-118 (1973)

Self-Regulating Polycondensations. II. A Study of the Order Present in Polyamide-Hydrazides Derived from Terephthaloyl Chloride and p-Aminobenzhydrazide

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ABSTRACT

The problem of chemical order of polyamide-hydrazides prepared from terephthaloyl chloride with an unsymmetrical monomer, p-aminobenzhydrazide, is discussed. An NMR method for identifying the molecular structure of species formed in the early stages of polycondensation has enabled the course of a polymerization to be followed during this time and the final degree of order to be predicted qualitatively. These studies have provided a demonstration that the structure of these polymers can be controlled to a significant

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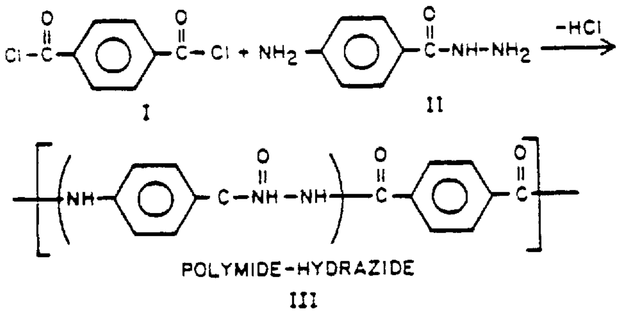
degree by appropriate variations in experimental conditions. But even under the most adverse conditions usually employed, polyamide-hydrazides are found to be at least "partially ordered" copolymers. The techniques developed for this study may find application in the study of other polymer forming reactions with monomers having two functional groups with dissimilar reactivities.

INTRODUCTION

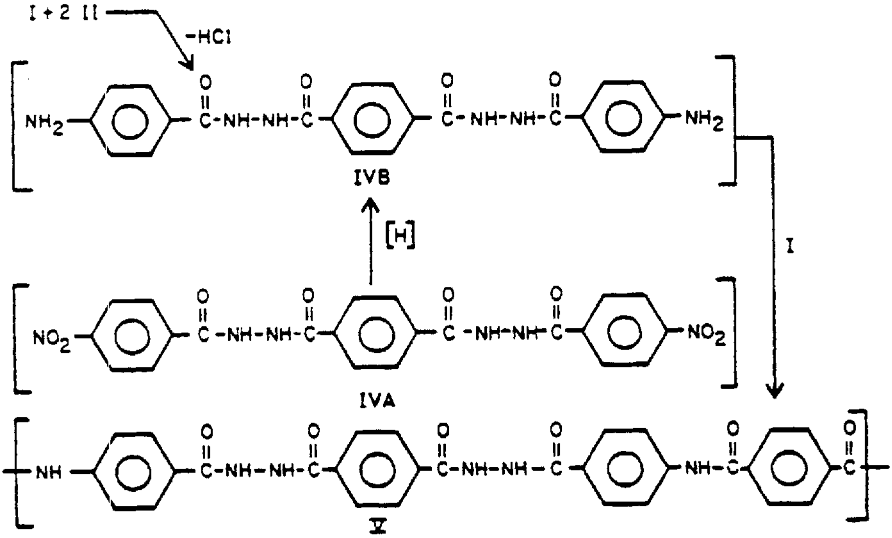
Aromatic polyamide-hydrazides [1] prepared by low-temperature solution polycondensation from diacid chlorides and aminobenzhydrazides might be expected to be copolymers of "limited order" [2] unless there exists an inherent difference in reactivity between the aromatic amine groups and the hydrazide groups of the unsymmetrical aminobenzhydrazide monomers. Because a hydrazide group is more nucleophilic than an aromatic amine group, it might reasonably be expected that the rate of reaction of the former would be considerably more rapid with an acid chloride than the latter. Hence the possibility exists for obtaining an ordered polyamide-hydrazide via a self-regulating polycondensation reaction [3] provided that other factors will allow these differences in reactivity to govern the course of the polycondensation.

In this paper we wish to report the results of our study of the reaction (Eq. 1) of terephthaloyl chloride (TCl), I, with p-aminobenzhydrazide (PABH), II, under a variety of experimental conditions to determine the degree of order in the polyamide-hydrazide obtained. Even under the most adverse conditions of polycondensation usually employed, the polyamide-hydrazide (III) is found to contain a substantial degree of order and can, at the very least, be referred to as a "partially ordered" copolymer. Order as used in this paper will refer to the regularity of placement of structural units along the polymer chain, i.e., "chemical order" will be discussed rather than "physical order" by which is meant the organization of polymer chain segments into crystalline and amorphous domains.

A wholly ordered polyamide-hydrazide [4], V, was prepared (Eq. 2) from IVB which in turn was synthesized [5] by reduction of the corresponding dinitro compound (IVA) or was obtained from the reaction of at least two equivalents of II with I [6].



(1)



(2)

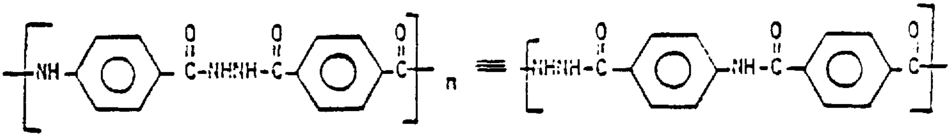
The direct polycondensation of I and II will be referred to here as a one-step reaction. The polycondensation of I with IVB will be referred to as a two-step reaction because III is isolated in a separate operation prior to use.

The various reactions and polymerizations were carried out in basic solvents such as dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), and hexamethylphosphorictriamide (HPT); in some cases an inorganic lithium salt such as lithium chloride was added to the solvent. The by-product of the polycondensation reactions was HCl, which complexes with the solvent to form a salt that enhances the solubility of the polymer in the polymerization media.

DISCUSSION

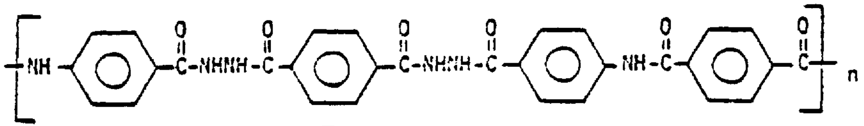
Types of Order

The structure of the polyamide-hydrazides is discussed here in terms of chemical order, i.e., the degree to which terephthaloyl chloride couples, either in a symmetrical or unsymmetrical manner, with the aminobenzhydrazide. There are two conceivable types of completely ordered polymers which could result from TCl and PABH in a one-step reaction:



VI

Uniform head-to-tail coupling

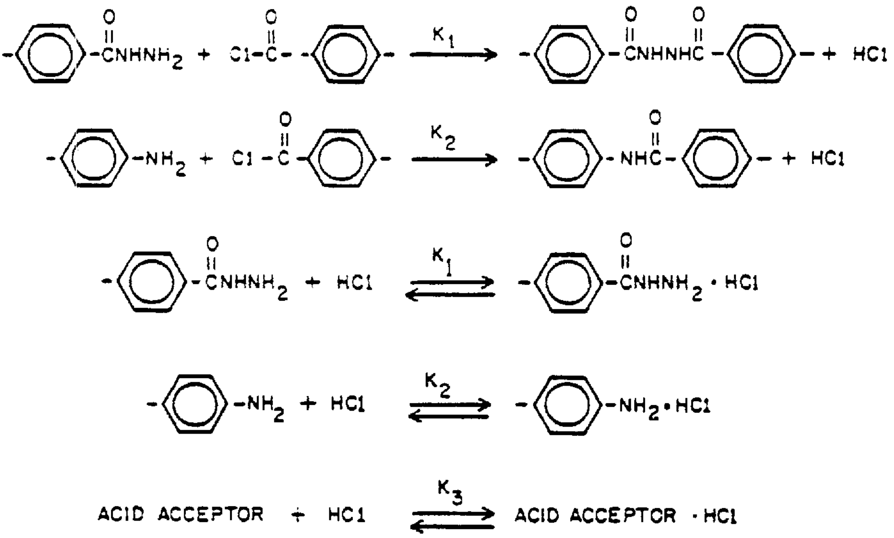


V

Alternating head-to-head and tail-to-tail coupling

Obviously, the only polymer structure possible from the two-step reaction described above is of the type shown for V.

Actually, the structure of polymers prepared by the one-step method is influenced by a number of factors other than the relative reactivities of the amine and hydrazide groups, e.g., the mode of addition of reactants, the presence of acid acceptors, diffusion, etc. The importance of these secondary factors can best be understood in terms of the major types of chemical reactions which occur in these polycondensation reactions. These are outlined in Scheme 1.

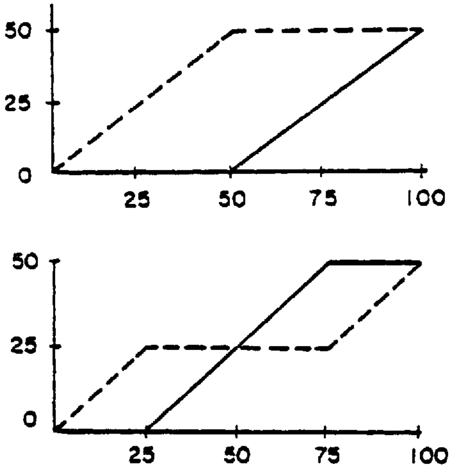


SCHEME 1.

The amount of head-to-head, head-to-tail, and tail-to-tail coupling will depend on the k_1/k_2 ratio if the diacyl chloride is added to a solution of the aminobenzhydrazide. If the inverse addition is employed and carried out sufficiently slowly, the aminobenzhydrazide would be expected to react completely during the early stages of polymerization and the effects of k_1/k_2 would go unnoticed. Second, the course of the reaction will become influenced by the base.HCl equilibria since the amine salts do not react with acyl chlorides [7]. Thus the presence of acid acceptors or the use of a basic solvent would be expected to affect the manner in which the polymer chains are formed. Finally, if the ratio of k_1/k_2 is extremely large or extremely small, then one type of condensation between I and II will predominate and an essentially ordered polymer will be the result.

The total possibilities for the effects of reaction conditions and relative reactivities on incipient structure appear quite large. Since any competitive chemical reactions will lead to some degree of disorder in the final polymer structure, one must select experimental conditions which maximize the effect of any difference in the reactivity of the amine and hydrazide groups of the aminobenzhydrazide toward terephthaloyl chloride if a maximally ordered polymer is desired.

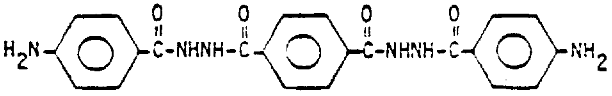
If the reactivity of the hydrazide end of PABH is much greater than that of the amine end, i.e., $k_1 \gg k_2$ (as seems reasonable on the basis of preliminary rate measurements) and the reactivity of the unreacted half of the terephthaloyl moiety is essentially equivalent to that of unreacted terephthaloyl chloride, then chemical order can be created by a slow addition of the diacyl chloride to the aminobenzhydrazide under conditions of ideal mixing. The two possible reaction pathways to the ordered polymer V under these conditions can best be understood from graphical illustrations indicated in Situations 1 and 2 of Scheme 2.



SCHEME 2. Situation 1 (top): The reaction of terephthaloyl chloride with p-aminobenzhydrazide in the presence of an efficient acid acceptor "B." Situation 2 (bottom): The reaction of terephthaloyl chloride with p-aminobenzhydrazide in the absence of an efficient acid acceptor. (The term "efficient acid acceptor may be defined as a material which would preferentially and completely tie up the HCl when in competition with the very basic hydrazide groups. An acid acceptor which would actually meet these requirements would be remarkable.) For both situations the abscissas are the percent of that amount of terephthaloyl chloride required for polymer (% completion of polymerization), and the ordinates are the per cent amine and hydrazide ends reacted divided by 2. (- -) Hydrazide ends; (——) amine ends.

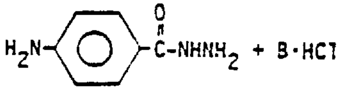
According to the reaction sequence of Situation 1, the aminobenzhydrazide would exist in the following forms during the polymerization:

At 25% completion of polymerization, 50% as



III

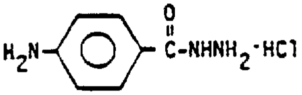
and 50% as



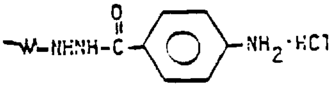
At 50% completion of polymerization, 100% as III + B.HCl. From this point, perfect chemical order is inevitable.

According to the reaction sequence of Situation 2, the aminobenzhydrazide is observed in the following forms during the polymerization:

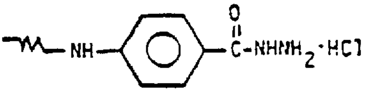
At 25% completion of polymerization, 50% as III and 50% as



At 50% completion of polymerization, 50% as

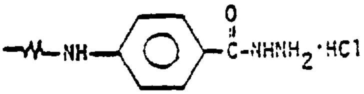


and 50% as

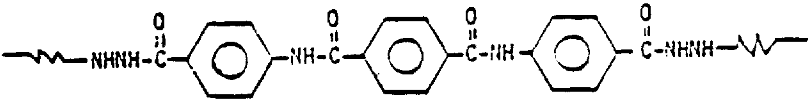


This scheme now requires an entirely preferential reaction on amine ends before further reaction on hydrazide ends.

There, at 75% completion of polymerization, 50% as



and 50% as



From this point, perfect order is obtained.

It is apparent that the only requirement for the formation of a wholly ordered polymer of type V is that only one type of end group should react completely with the diacyl chloride at a given point in time.

For the reaction sequence to follow that outlined in Situation 2 from 50% to completion, a nearly quantitative preference for amine ends must be exhibited by the acyl chloride groups. Such a preference can occur only if the dissociation of the hydrazide salt is almost nonexistent. There is the possibility that differences in association can be offset by the differences in reactivity to such an extent that the hydrazide remains competitive in spite of large differences in association constants. Nevertheless, if one could effectively achieve nondissociation of the hydrazide salts, then a wholly ordered polymer would be almost unavoidable.

Since the equilibrium of HCl among all the basic sites in the reaction mixtures could very well effect a deviation from the ideal situation described in Situation 2, the method of choice for optimum order would appear to be as described in Situation 1. Unfortunately, however, there are practical problems involved with the use of strongly basic materials in the polymerization mixtures. In DMAc, the usual basic solvent employed in these reactions, the hydrochloride salt of a strong organic base (such as triethylamine) usually crystallizes. Furthermore, removal of HCl from the

DMAc system gives rise to a lower solvating power of the solvent, leading to the possibility of partially precipitated polymer. In either system the diffusion problem caused by the increasingly larger molecules which form in the reaction mixture could effect deviations from ideal behavior. Consequently neither situation appears to be free of effects which could cause less than perfect order.

Examination of Chemical Order

A method for determining the chemical compositions of oligomers in the presence of amine and hydrazide salts formed by a slow addition of the diacyl chloride (TCl) to a solution of the PABH would enable one to determine the respective percentages of reaction on the amine and hydrazide ends of the aminobenzhydrazide as a function of added diacyl chloride. This determination of the reaction course during the early stages of polymerization would enable one to estimate the relative reactivities of the amine and hydrazide ends (i.e., k_1/k_2) and to predict, at least qualitatively, the degree of order in a polymer that results from completion of the addition of the stoichiometric amount of diacyl chloride required for high molecular weight polymer. A positive correlation of this predicted order with that obtained from electron diffraction and x-ray studies would provide credence to the assignment of the type and degree of order for a polymer made in a particular way.

Two techniques have been developed for studying the chemical composition of these reaction mixtures. One is based on the titration of reacted hydrazide groups (as weak acids) with tetrabutylammonium hydroxide [8]. The other technique utilizes nuclear magnetic resonance spectroscopy (NMR) [9]. The NMR technique has been used for this study because it has allowed greater flexibility with the nonaromatic solvent systems used. The NMR technique is not useful, however, when an aromatic solvent is employed, and in such a case the titration method would be required. Reaction mixtures to which more than 50% of the theoretical diacyl chloride has been added have not been examined because of difficulties in analysis. Consequently, estimation of what the order of the polymer would be if the reaction were carried to completion were made on the basis of the analyses presented in Situations 1 and 2 (Scheme 2).

RESULTS

Chemical Order of Oligomers

The general reaction course during the early stages of polymerization could be deduced from the NMR data which indicated on the molecular level the precise manner in which the reacting molecules were condensing. The reaction curves for up to 50% completion of polymerization (b/a = 0.5; where b/a is the molar concentration ratio of diacyl chloride to aminobenzhydrazide in the original mixture) for six reaction conditions in which the TCl was added slowly to solutions of PABH are illustrated in Figs. 1-6. These conditions included the addition of the TCl as a solid or as a solution to solutions of the PABH in various solvents. (Note: When solid TCl was used it was always added to the reaction mixture all at once; the slow process of dissolution in the cold mixture realistically effected a slow addition of the reactant in these cases.)

Selected reactions which involved the use of other mixtures are also discussed below.

Figure 1 indicates that selective reaction during early stages of polymerization can be achieved by the addition of TCl as a solution in tetrahydrofuran (THF) to a DMAc solution of PABH. This system can most easily be interpreted in terms of Situation 2 (Scheme 2). Since the theoretical curve predicted by Situation 2 appears to be followed rather closely (but not exactly) up to b/a = 0.40, one must conclude that k_1 is inherently much greater than k_2. Calculations based on the data from this system have indicated that k_1/k_2 may be as high as 100/1 [10]. The apparent reversal in observed reactivities in the region from b/a = 0.25 to 0.40 may be explained on the basis of the more basic hydrazide groups being tied up with HCl as discussed earlier. This almost complete reversal in observed reactivities implies also that the hydrazide salt shows little tendency to dissociate.

At least two complicating factors can possibly explain the decrease in preferential reaction above b/a = 0.40. By this point the quantity of HCl which has been generated is almost equivalent to the remaining unreacted amine and hydrazide groups. Consequently the HCl equilibria discussed previously and the effects of reactivity differences for the unprotonated species may now be influencing the reaction course. Moreover, in addition, the actual size of the oligomers may have increased to such a point that molecular mobility is reduced, permitting diffusion

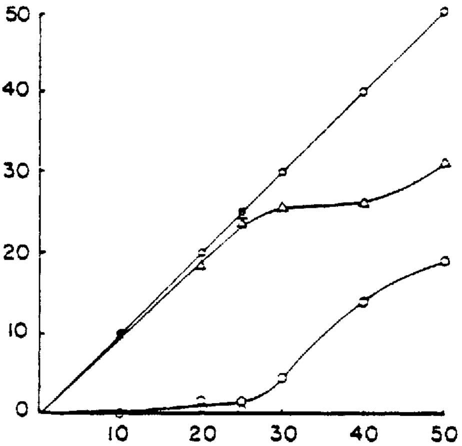


FIG. 1. Terephthaloyl chloride (TCl) added as a solution in tetrahydrofuran to a solution of p-aminobenzhydrazide (PABH). Abscissa: Per cent of that amount of TCl required for polymer (b/a x 100, where b/a is the molar concentration ratio of TCl to PABH present in the original mixture). Ordinate: Per cent amine and hydrazide groups reacted divided by 2. (△) Hydrazide groups (by difference); (o) amine groups; (o) total.

to exert a noticable effect. It appears reasonable that strong diffusion control would tend to equalize the apparent k_1 and k_2. Thus, if an acyl chloride molecule cannot diffuse freely, it is most likely to react with the nearest free amine or hydrazide irrespective of any large difference in their reactivities.

In contrast to Fig. 1, Fig. 2 indicates that when terephthaloyl chloride is added as a solid to DMAc solutions of PABH over a range of concentrations, a relatively low degree of reactive selectivity is attained. Since it was demonstrated that k_1 is inherently much larger than k_2, we must conclude that these reaction conditions favor diffusion rather than kinetic control. In other words, the reaction most likely occurs near the surface of the slowly dissolving TCl crystals and not further out in solution.

Figure 3 represents a case which is intermediate between those of Figs. 1 and 2. The addition of the diacid chloride in THF apparently allows for more adequate mixing before reaction occurs.

Curiously, the substitution of a 5% solution of lithium chloride in DMAc for pure DMAc enhances the selectivity of the reaction

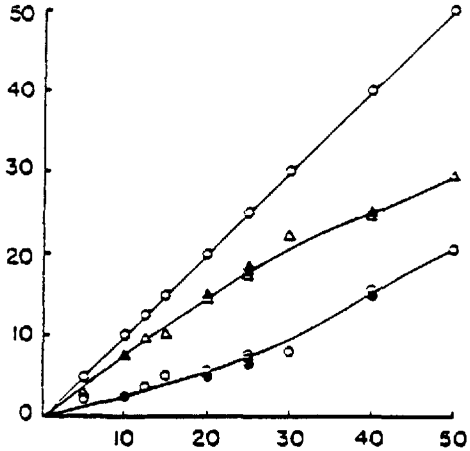


FIG. 2. TCl added as a solid to a solution of PABH in dimethylacetamide. Abscissa and ordinate as in Fig. 1. (o = 0.8 M PABH; ● = 0.278 M PABH; ● = 0.14 M PABH; ▲ = 0.278 M PABH.) (△) Hydrazide groups (by difference); (o) amine groups; (o) total.

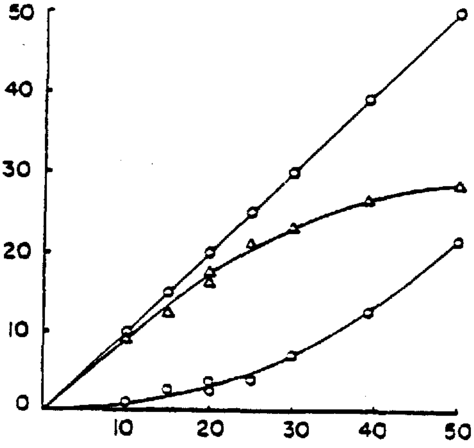


FIG. 3. TCl added as a solution in dimethylacetamide to a solution of PABH in dimethylacetamide. Abscissa, ordinate, and symbols as in Fig. 1.

when the TCl is added as a solid (Fig. 4). Since DMAc/LiCl acts in these reactions as a more potent solvent than DMAc, one might speculate that the enhanced selectivity may be a result of less

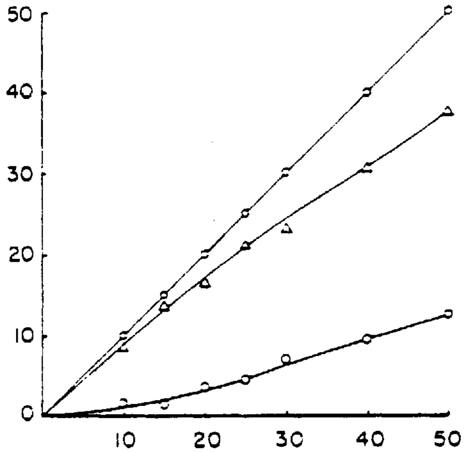


FIG. 4. TCl added as a solid to a solution of PABH in dimethylacetamide containing 5% dissolved LiCl. Abscissa, ordinate, and symbols as in Fig. 1.

diffusion control in the better solvent. This explanation may be valid, in part, but the most significant aspect of this curve is the high degree of reaction on hydrazide ends at b/a = 0.50. Since at this point 75% of the hydrazide ends have reacted, something in the system must have acted as a better acid acceptor than merely DMAc alone. After analysis of the solvent indicated the absence of a strong base, a potentiometric technique demonstrated that the addition of LiCl to DMAc does indeed increase the acid accepting ability of the solvent [8].

Further credence may be given to this basicity argument for the DMAc/LiCl system because the curve for the reaction with the unusually basic HPT system [11] (Fig. 5) is essentially superimposable with that in Fig. 4. As would be expected, the curves for both of these systems indicate that the reactions are tending to follow the reaction pathway described in Situation 1 (Scheme 2) rather than that of Situation 2.

Figure 6 indicates that the NMP system also is intermediate between those described in Figs. 1 and 2. The general shape of this curve suggests not only a less strongly diffusion controlled reaction than that observed in DMAc (Fig. 2), but also at least a comparable degree of relatively poor acid accepting ability of the solvent since a strong break occurs in the curve around b/a = 0.25.

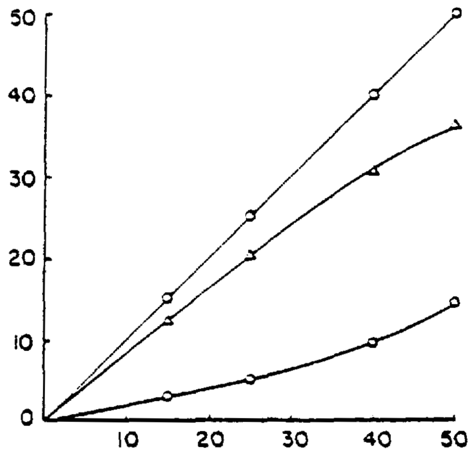


FIG. 5. TCl added as a solid to a solution of PABH in hexamethylphosphorictriamide. Abscissa, ordinate, and symbols as in Fig. 1.

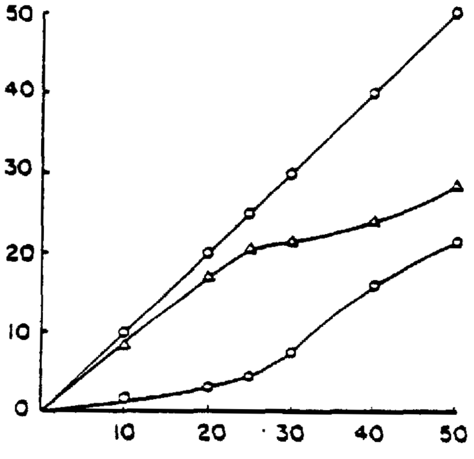


FIG. 6. TCl added as a solid to a solution of PABH in N-methylpyrrolidone. Abscissa, ordinate, and symbols as in Fig. 1.

A few reactions which were carried out in the presence of triethylamine have indicated in a general sense that a more preferential reaction can sometimes be effected by this method. However, the reproducibility of these experiments up to this point has been poor. Reasons for this lack of reproducibility are unknown.

An interesting series of reactions was carried out in the presence of anhydrous HCl. Specifically, a sufficient quantity of a standard solution of dry HCl in DMAc was added to a DMAc solution of PABH to tie up (theoretically) all of the hydrazide groups as salts. This solution resembles that of a reaction mixture in which $b/a = 0.25$ and in which all the reaction up to that point had occurred on hydrazide groups (theoretical Situation 2, Scheme 2). All of the aromatic amine groups would be expected to be free to react, while the hydrazide groups would be either reacted or tied up as salts. To this "PABH.HCl" solution was then added 25% of the theoretical amount of TCl required for polymer formation. Out of a maximum of 50%, the measured amounts of aromatic amine ends reacted with 28 and 36% for additions of the acid chloride as a solid and in THF, respectively. Furthermore, addition of a similar portion of the TCl as a solid to a "PABH.2HCl" solution resulted in 41% of the aromatic amines reacting. These results confirm not only the existence of an equilibrium of HCl among all the basic centers in the reaction system, but also that additional HCl appears to suppress hydrazide salt dissociation to a much greater extent than the amine salt dissociation.

Chemical Order of Polymers—Prediction and Confirmation of Relative Order

If one assumes that the experimentally observed deviations from those theoretical pathways which appear necessary for obtaining an ordered polymer, V, indicate achieving less than complete order, then no polymer prepared by the one-step processes reported here attained the perfect order of the polymer prepared by the two-step route. Nevertheless, these studies suggest that the polymers which would result from completion of the TCl addition would have chemical order in a range from relatively high (THF case, Fig. 1) to rather low ($TCl_{(s)}$/DMAc case, Fig. 2). Therefore, showing that by controlling the manner and environment in which TCl and PABH are brought together, one can control the chemical order of the polymer to a quite significant degree.

Polymer prepared by the addition of the TCl as a solid to solutions of the PABH in HPT (Fig. 5) would be expected to have a chemical order which is intermediate between the two extremes mentioned above. Likewise, the polymer prepared from DMAc solutions of both reactants under the conditions described in Fig. 3 would be expected to exhibit this intermediate degree of order. The curves in Fig. 4 show that a polymer more ordered than those made by the methods described in Figs. 3 and 6 could be produced. Nevertheless, the order would be expected to be less than that of polymer made according to the method described in Fig. 1. A polymer prepared by the addition of solid TCl to PABH in NMP (Fig. 6) would be expected to be ordered almost as well as one made by the addition of a THF solution of TCl to a DMAc solution of the PABH.

Electron diffraction studies on annealed polymer films [12] have confirmed that one does indeed obtain polymers with widely different degrees of chemical order as a consequence of varying the reaction conditions along lines similar to those shown in Figs. 1-6. Such electron diffractograms are reproduced in Ref. 5.

EXPERIMENTAL

A 250-ml three-necked conical flask equipped with a mechanical stirrer, nitrogen inlet, drying tube, and dropping funnel (where necessary) was dried completely by the application of a Bunsen flame before introduction of the reactants. Dry DMAc (DuPont), p-aminobenzhydrazide (Gallard-Schlesinger), and terephthaloyl chloride (Hooker) were used as solvent and monomers.

Kinetic Studies

NMR spectra were determined on a Varian A60 NMR spectrometer; integrals were averages of 5-10 scans. A few drops of trifluoroacetic acid were added to the samples prior to examination. All solvents were previously dried over 3 Å molecular sieves and the same source of raw materials were used throughout this study. Typical reactions are described below.

Acid Chloride Added as a Solid

A solution of 1.051 g (0.00695 mole) of PABH in 23.7 ml of DMAc was chilled to about -10° by the application of an ice-salt bath for 30 min. To this chilled solution was added (with vigorous stirring) 0.353 g (0.00174 mole) of TCl by means of a slender funnel of weighing paper which was held slightly above the liquid surface. The reaction was stirred for about 2.5 hr during which time the acid chloride slowly dissolved, the ice melted, and the bath slowly warmed up to room temperature. The pale yellow solution was then examined by NMR.

Reaction in the Presence of Triethylamine

A solution of 1.051 g (0.00695 mole) of PABH in 23.7 ml of DMAc was chilled to about -10° by the application of an ice-salt bath for 30 min. To this rapidly stirred solution was added 0.54 ml (0.39 g, 0.0039 mole) of distilled triethylamine followed by 0.353 g (0.00174 mole) of TCl. Stirring was continued for 2.5 to 3 hr during which time the ice melted and the bath generally warmed up to room temperature. The fine white precipitate of triethylamine hydrochloride was removed by filtration and washed with dimethylacetamide. The collected filtrate was then examined by NMR.

Reaction in DMAc/LiCl

Reactions carried out in DMAc/LiCl were identical to those done in DMAc except that a 5% solution of LiCl in DMAc was substituted for pure DMAc.

Reaction in HPT

Reactions carried out in HPT were identical to those carried out in DMAc except that the PABH solutions were chilled only to 0° rather than to -10°. In some cases a small quantity of 5% LiCl in DMAc was added after the reaction was complete in order to redissolve small amounts of crystallized material.

Reaction in NMP

A solution of 1.08 g (0.00714 mole) of PABH in 25 ml of distilled NMP was chilled to 0° by the application of an ice-water bath for 30 min. To the chilled solution was added 0.36 g (0.00178 mole) of TCl with vigorous stirring. The ice-water bath was allowed to warm gradually to room temperature over a period of 2.5-3 hr. The clear solution was examined immediately by NMR; otherwise a precipitate which does not always redissolve in NMP sometimes form on standing.

TCl Added in THF—Preparation of the Symmetrical Diamine III

A solution of 1.051 g (0.00695 mole) of PABH in 23.7 ml of DMAc was chilled to about -10° by the application of an ice-salt bath for 30 min. A solution of 0.353 g (0.00174 mole) of TCl in 25 ml of

THF was then added slowly (with vigorous stirring) over a period of 5-10 min and the dropping funnel was then washed down with an additional 5 ml of THF. About 5 min after the addition was complete the ice-salt bath was removed. Fifteen minutes later, vacuum was applied to the reaction mixture in order to remove the THF. The mixture was stirred overnight under house vacuum during which time a white solid (identified as diamine III by NMR and by a mixture melting point determination with an authentic sample [5]) precipitated slowly. A clear solution was effected by the addition of 5 ml of a 5% solution of LiCl in DMAc. This solution was then examined by NMR.

Note that in all of the THF additions, the volume of THF was constant regardless of the amount (up to 50% of theoretical for polymer formation) of TCl used. In the cases where 40 and 50%, respectively, of the TCl required for polymer had been added, a gummy material "oiled out" of solution. This material dissolved as the THF was removed. These two reactions were later carried out in one phase with a more concentrated solution of acid chloride in THF, but the analysis results were identical to those obtained earlier.

TCl Added in DMAc

Reactions which involved the addition of TCl in DMAc were usually carried out according to the procedure described above except that DMAc was substituted for THF, no vacuum was applied, and the solutions remained homogeneous. When the quantities of DMAc specified in the section were halved, little difference in experimental results was noted.

Polymer Preparations

TCl Added as a Solid

Polymers can be prepared by the general procedure described in the first example in the kinetics experimental section, with the exception that equimolar quanties (0.00695 mole) of both acid chloride and aminobenzhydrazide are allowed to react. Solvents for this procedure have included DMAc, DMAc/5% LiCl, NMP, and HPT.

Addition of TCl in THF

A solution of 1.077 g (0.00712 mole) of PABH in 25 ml of a 5% solution of LiCl in DMAc was chilled to about -10° by application of an ice-salt bath for 30 min. A solution of 1.446 g (0.00712 mole) of TCl in 30 ml of THF was added at a moderate rate with rapid stirring. After about 2/3 of the acid chloride solution had been added, a phase separation was observed in the reaction mixture. The reaction mixture was stirred for 5 min before the remaining acid chloride solution was added rapidly. The dropping funnel was then rinsed down with an additional 20 ml of THF. Immediately a sticky-looking solid formed into a ball. The stirred reaction mixture was then allowed to warm slowly to room temperature while the THF was removed by either a rapid sweep of nitrogen or by vacuum. After 2 hr a very viscous polymer solution had formed which was diluted with an additional 35 ml of 5% LiCl in DMAc. This solution was suitable for subsequent conversion into fibers and films.

A polymer was also prepared similarly in pure DMAc.

SUMMARY AND CONCLUSIONS

The significance of this study lies not only in the demonstration that more than one type of structure is possible in one-step polymerizations of TCl with PABH, but also that this structure can be predicted and actually controlled (within certain limits) by the proper choice of experimental conditions. The techniques developed for the study of this system will surely find application in the study of other one-step reactions with monomers having two functional groups with dissimilar reactivities.

ACKNOWLEDGMENTS

We wish to acknowledge the outstanding technical assistance of our co-workers, Mrs. Nancy J. Wildman and Mr. E. W. Wilburn. The development of the alternative titration technique by Drs. R. G. Garmon and W. W. Lanier, and Dr. V. F. Holland's electron diffraction studies were particularly valuable. The interest of, suggestions from, and discussions with Drs. J. J. Hermans and W. F. Hamner are sincerely appreciated.

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