Three-dimensional polycondensation of monomers with ionomer-type interactions

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The three-dimensional polycondensation of bifunctional hexamethylene diamine and trifunctional guanidine hydrochloride is studied. It is shown that the properties of this process do not follow the classical Flory theory. One of the most interesting features is the dependence of the critical extent of the polycondensation (i.e. the gel point) on the synthesis temperature. It is supposed that the reason for this is the different reactivity of the functional groups of guanidine hydrochloride and the different temperature coefficient of reactivity. As a result, some parts of the functional groups are excluded from the reaction. It is supposed that the reason for this is the ionomer character of the guanidinium links in the linear chains. Due to dipole–dipole interactions the ion pairs associated with the third functionality of these links aggregate into multiplets. Thus, reaction groups turn out to be effectively sterically screened and their ability to enter into the reaction with the formation of branching points becomes restricted.

(Keywords: polycondensation; ionomer; temperature)

INTRODUCTION

The classical theory of three-dimensional polycondensation was proposed by Flory in 1953[1]. This theory was based on the following main assumptions: the independence of the reactivity of end functional groups on the length of the chains and of the topology of macromolecules; the absence of intramolecular cyclization reactions; and the reactivity of a functional group of a polyfunctional monomer does not depend on the substitution of neighbouring functional groups.

If these assumptions are obeyed in the course of polycondensation, randomly branched macromolecules are formed with a statistical distribution of chain lengths between branching points. At some stage in the reaction the molecular weight and polydispersity of the branched macromolecules increase considerably and a gel is formed (at the gel point the weight-average molecular weight, $\bar{M}_w$, tends to infinity).

The Flory theory describes a large amount of experimental data[2,3]; however, in some papers significant deviations from the Flory theory have been reported[4,5]. One of the possible reasons for these deviations may be strong interactions between potentially reactive groups in the process of polycondensation: Coulomb interactions, hydrogen bonds, dipole–dipole interactions, etc. In particular, if reactive groups are charged and the polycondensation takes place in a non-polar medium, ion pairs are inevitably formed. Thus, the macromolecules should have some ionomeric properties. It is well known that the dominating factor which defines the structure of ordinary ionomers is the strong attraction of ion pairs which leads to the formation of multiplet structure[6–9]. It is clear that this type of structure could also be formed in the process of polycondensation. In this case, reactive groups are included in the multiplets, and steric hindrance in the vicinity of these groups becomes very pronounced, which significantly influences the polycondensation and causes large deviations from classical theory.

The present paper is devoted to the experimental study of one system of this kind. We will describe the experimental results on the three-dimensional polycondensation of bi- and trifunctional monomers with ionic groups: hexamethylene diamine (HMDA) and guanidine hydrochloride (GHC). We will show that the key factor for the polycondensation laws for this system is the ionic character of the trifunctional GHC. To our knowledge the influence of ionomer effects on polycondensation behaviour has not been discussed in the literature so far.

EXPERIMENTAL

The synthesis of poly(hexamethylene guanidine hydrochloride) (PHMG) was performed by means of high temperature polycondensation of a bifunctional HMDA with trifunctional GHC in the melt of monomers using the methods described in reference 10. The reaction takes place according to *Scheme 1*. The GHC cation is highly symmetric and stable, and is bound electrostatically to the chlorine anion. All three NH groups of GHC are equivalent[11], therefore the excess positive charge is

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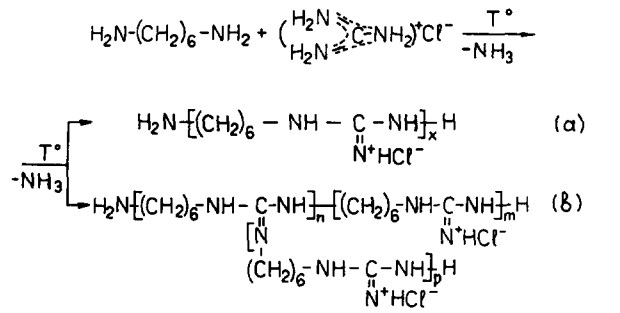

Scheme 1 General scheme of the reaction under consideration

equally distributed between these groups and their initial reactivities are the same. However, it is evident that after the substitution of two functional groups of GHC the proton becomes localized belonging to the third, unreacted functionality (*Scheme 1a*). Thus, the subsequent branching reaction (*Scheme 1b*) involves the participation of a strongly charged group. It is possible to change the following parameters in the synthesis: the duration of the reaction, the composition of the initial melt of monomers and the synthesis temperature.

Our main aim is to study the end products of the reaction. Therefore, it is necessary to determine the duration of the synthesis, i.e. the time after which the molecular mass characteristics of the reaction product are no longer time dependent. To do this, we stopped the reaction at different stages by cooling the samples to room temperature where the polycondensation reaction does not take place. These samples were further dissolved in a large amount of an aqueous solution of a low molecular weight salt (0.3 mol l^{-1}) to screen the electrostatic effects. In *Figure 1* the values of $\bar{M}_w$ and the amount of gel, W_g, are plotted as functions of time of synthesis, t. The non-monotonous change of $\bar{M}_w$ of the soluble polymer with time is a consequence of the appearance of gel: maximum $\bar{M}_w$ corresponds to the critical point of gel formation which occurs at $t=t_c$. At $t<t_c$ the value of $\bar{M}_w$ increases with time of the reaction, and at $t=t_c$, $\bar{M}_w$ tends to infinity, while at $t>t_c$ the gel is formed. Therefore, the value of $\bar{M}_w$ corresponds to the sol fraction and decreases with the increasing amount of gel fraction. It can be seen that the parameters $\bar{M}_w$ and W_g are practically constant at $t>10$ h. Approximately at this time (or even earlier) the release of ammonia stops. Thus, all further results were obtained for the reaction exceeding 10 h.

The composition of the initial monomer melt, $\mathscr{X}=N_b/N_a$ (where N_a and N_b are the molar fractions of the trifunctional GHC and bifunctional HMDA, respectively), was changed from equimolar to stoichiometric, i.e. from $\mathscr{X}=1$ to 1.5. This is the most interesting region, because at $\mathscr{X}<1$ the molecular mass of the final product decreases considerably and at $\mathscr{X}>1.5$ the characteristics of the final product are practically constant.

The synthesis temperature, T, was chosen to be 165, 180 and 200°C.

The fractionation of PGMG was performed with a preparative chromatographic column (1 m long and 10 mm diameter). Sephadex G-50 with particle dimensions of 100–300 μm was used as a sorbent. A 20% aqueous polymer solution (10 ml, 2 g) was loaded into the upper part of the column. The elution of fractions was achieved by adding distilled water until the polymer was completely washed out of the column; 10–15 fractions were usually obtained. A refractometer was used as the detector. The amount of polymer in a given fraction was determined by drying 2 ml of aqueous solution. The loss of polymer in the fractionation process is not large ($\leqslant$1.4–5.0 wt%).

The viscosity of dilute polymer solutions, polymer fractions and sol fractions after separation of the gel were determined using an automatic viscosimeter (AVC 400, Schott Gerate, Germany) at 25±0.05°C. Since PHMG is a polycation in water, the measurements were performed in 0.3 M aqueous NaCl solutions to suppress the polyelectrolyte effect. The measurements were made for four to six concentrations in the range $c=0.5$–3.0 g dl^{-1}. Using a double extrapolation of η_{sp}/c and $\ln(\eta_{sp}+1)/c$ to infinite dilution the intrinsic viscosity $[\eta]$ was determined [$\eta_{sp}=(\eta-\eta_o)/\eta_o$, where η and η_o are the viscosities of the solution and solvent, respectively].

The $\bar{M}_w$ of the PHMG samples and of the sol fractions were calculated from the sedimentation data using the non-equilibrium method[12]. The experiments were performed on an analytical ultracentrifuge (MOM 3180, Hungary) at 25±0.1°C for four to five concentrations of PHMG (0.5–1.0 g dl^{-1}). By means of extrapolation of the inverse of the apparent $\bar{M}_w$ calculated for finite concentrations to infinite dilution the real value of $\bar{M}_w$ was determined. Measurements of the partial specific volume, $\bar{v}$, of the polymer in solution, which is necessary to calculate the molecular weight from the sedimentation data, were performed by pycnometry. Within the limits of accuracy the value of $\bar{v}=0.815$ ml g^{-1} was shown to be the same for all the samples studied.

The amount of gel fraction was determined by means of the following procedure. At the end of the reaction and after cooling the samples to room temperatures excess distilled water was added to the reaction product with subsequent mixing at 50°C for 8 h. Then, the residue was filtered using a Shott's filter N4, and was washed with hot (80°C) distilled water and dried in a vacuum at 80°C to constant weight. The soluble fraction was tested for any remaining microgel which may penetrate the Shott's filter by means of centrifugation using an analytical centrifuge (25 000–30 000 rev min^{-1}) for 3 h. If any microgel was found, its amount was determined and added to the gel fraction.

Swelling of the gel fraction was performed using the following method. After drying the gel fraction, the gel was put in special vessels with a porous base which were placed inside a thermostatically controlled container. Distilled water was added to the container, and the system was then heated to 40°C. At this temperature the gel fraction was stored in the hermetically sealed container,

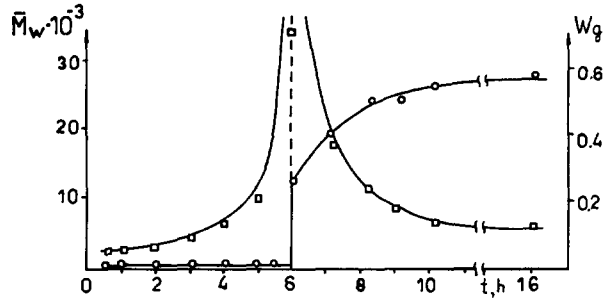

Figure 1 Plot of $\bar{M}_w$ and W_g of sample no. 9 (*Table 1*) *versus* the synthesis time, t

and the vessel containing the gel was periodically weighted.

RESULTS AND DISCUSSION

The conditions of synthesis, the molecular characteristics and the amount of gel of PHMG, synthesized at different temperatures and different mole compositions of monomers are presented in *Table 1*.

Analysis of the data allows us to draw some conclusions about the influence of the synthesis conditions on the molecular characteristics of PHMG and the amount of gel formed. The first effect which should be noted when considering the experimental data is the dependence of the critical composition of the monomers, $\mathscr{X}$, at which the beginning of gel formation is observed, and of the limiting amount of gel on the synthesis temperature (*Figure 2*). Moreover, the amount of gel in the investigated temperature range does not reach 100%. As can be seen from *Figure 2*, the experimental dependence of W_g on $\mathscr{X}$ differs essentially from the curve obtained according to the Flory theory[1].

The second specific feature of this process is the fact that at some definite conditions only oligomeric and nearly linear products are formed as a result of the polycondensation of bi- and trifunctional monomers. This is the case, for example, for samples 1 and 2 (*Table 1*), which were synthesized at 165°C with equimolar (or close to equimolar) monomer composition. As can be seen from *Table 1*, the molecular weight distribution (*MWD*) of these samples corresponds to the most probable distribution with the polydispersity coefficient $\bar{M}_w/\bar{M}_n \cong 2$. At the same time, for the other polymers $\bar{M}_w/\bar{M}_n \gg 2$.

As can be seen from *Table 2* and *Figure 3*, samples 1 and 2 are characterized by the Mark–Kuhn–Houwink dependence with the exponent $a=0.59$, lying in the interval 0.5–0.8. This interval is characteristic for linear polymers in a thermodynamically good solvent. For other samples this dependence becomes weaker and is characterized by the value $a<0.5$ (except for sample 10 which corresponds to very small molecular weights). This fact is a usual manifestation of the branched character of macromolecules[1]. These results can be interpreted in such a way that for samples 1 and 2 only two functional groups of the trifunctional monomer enter into reaction with the formation of a linear polymer, with the probability of the third functional group entering into the reaction being much lower, and thus branching is suppressed.

Another specific feature of the behaviour of the polymers studied was noticed when considering hydrodynamic properties of narrow fractions of PHMG polymers in aqueous NaCl solutions. As can be seen from *Figure 3*, if the molecular weights of the fractions are equal the value of $[\eta]$ generally increases with an increase in the synthesis temperature. Moreover, the swelling of gel fractions of samples which were synthesized at 200°C exceeds that of samples obtained at 165°C (*Table 3*). These facts can be explained if we assume that the increase in the synthesis temperature leads to an increase in the distance between junction points in the branched macromolecules. In its turn, this assumption is valid if mainly linear products are formed in the first stage of the reaction (the higher the temperature, the quicker linear chains are formed), and branching occurs only at the later stage (with some delay).

All the features described above of three-dimensional polycondensation of GHC, containing the ionic group, with HMDA show that there is an essential deviation in the process under investigation from the classical Flory theory for the formation of branched structures with the participation of polyfunctional compounds. We think

Table 1 Synthesis conditions, molecular parameters of the sol fraction and weight fractions of the gel for PHMG

Sample no.	$\mathscr{X}$	Synthesis temperature (°C)	$[\eta]$ (dl g^{-1})	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n{}^a$	W_g	$\bar{M}_{w,o}$ ($\times 10^{-3}$) Eqn (3)	$\bar{M}_{w,o}$ ($\times 10^{-3}$) Eqn (4)
1	1.00		0.042	2.2	2.0	0	2.2	
2	1.05		0.050	3.4	2.1	0	3.2	
3	1.10		0.056	5.3	7.0	0	3.4	
4	1.125		–	11.5	–	0.03		2.9
5	1.13	165	0.060	–	–	0.01		
6	1.15		0.079	9.7	–	0.33		
7	1.20		0.064	11.8	3.7	0.43		
8	1.30		0.110	–	–	0.45		
9	1.50		0.061	7.5	–	0.45		
10	0.95		0.038	1.7	1.9	0		
11	1.00		0.054	8.0	2.8	0	5.2	4.0
12	1.05		0.054	7.7	–	0		
13	1.10	180	0.070	9.8	–	0.05		
14	1.15		0.066	9.0	–	0.56		
15	1.20		0.087	–	–	0.62		
16	1.30		0.082	11.5	–	0.65		
17	1.50		0.042	–	–	0.67		
18	1.00		0.061	12.5	3.0	0	8.0	7.2
19	1.03		0.154	–	–	0.01		
20	1.05		0.150	43.0	3.3	0.18		
21	1.10	200	0.099	18.7	–	0.60		
22	1.15		0.060	4.5	–	0.72		
23	1.20		0.082	–	–	0.83		
24	1.30		0.054	–	–	0.85		
25	1.50		–	–	–	0.86		

The data on sol and gel fractions refer to samples after a reaction period of 10 h

[a] $\bar{M}_n$ was calculated from the fractionation data

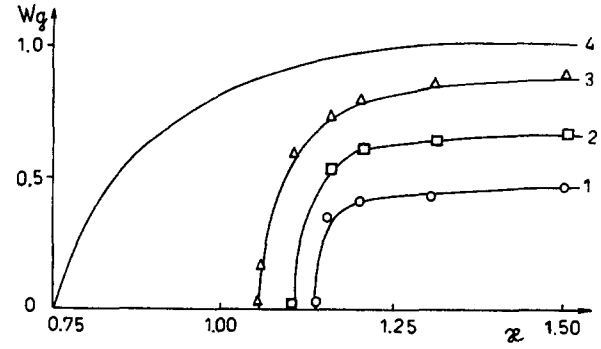

Figure 2 Plot of W_g as a function of $\mathscr{X}$. The synthesis was performed at 165°C (1), 180°C (2) and 200°C (3). Curve 4 is calculated in accordance with Flory theory[1]

Table 2 Parameters of the Mark–Kuhn–Houwink relation $[\eta] = K_\eta M^a$ for PHMG samples in 0.3 M aqueous NaCl solution at 25°C

Sample no.	Synthesis temperature (°C)	$\mathscr{X}$	K_η ($\times 10^4$)	a
1	165	1.00	0.46	0.59
2	165	1.05	0.46	0.59
3	165	1.10	2.08	0.39
7	165	1.20	4.08	0.34
9	165	1.50	4.08	0.34
10	180	0.95	0.46	0.59
11	180	1.00	2.08	0.39
18	200	1.00	4.88	0.32
20	200	1.05	4.88	0.32

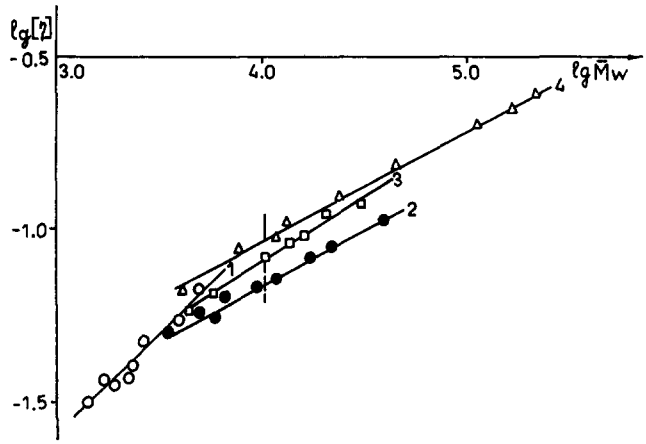

Figure 3 Log–log relations between $[\eta]$ and $\bar{M}_w$ for PGMG fractions: (1) 165°C, $\mathscr{X} = 1$; (2) 165°C, $\mathscr{X} = 1.5$; (3) 180°C, $\mathscr{X} = 1$; (4) 200°C, $\mathscr{X} = 1$

that these deviations are connected to the fact that the third functional group of GHC (=NH.HCl) is an ionic pair and thus has lower reaction ability than the first two groups. Indeed, in the melt, in the absence of solvent, these ion pairs are known to be grouped in multiplets[6]. In this case, functional groups turn out to be embedded within multiplets (*Figure 4*), and this limits the probability of reaction involving these functional groups and the formation of branching centres.

The lowering of the reactivity of the third functional group can also be explained in terms of the recent theoretical approach of reference 8 according to which there should be a region of restricted mobility of the chain segments around each multiplet. Of course, under the condition of different reactivity of the functional groups the Flory theory should not be valid (see the assumptions of this theory given earlier).

To check the assumption that the low reactivity of the third functional group is connected with the formation of multiplets we synthesized PHMG in the presence of NaOH at 165°C and at equimolar monomer composition, i.e. in the conditions when the linear polymer is formed in the absence of NaOH. It turns out that it is enough to introduce 0.5 M NaOH per mole of GHC in order to obtain an almost completely crosslinked reaction product. This experimental fact can be explained by the destruction of the ionic pair due to the deprotonation of the imino group of the bisubstituted guanidinium. As a result, the ability of the third functional group of GHC to enter into reaction approaches that of the other two functional groups. This experiment is additional proof of the fact that when two functional groups of GHC are substituted and their charge is redistributed, a decrease in the reaction ability of the third functional group occurs. In other words, the deviations from the Flory theory seem to be due to the ionic character of the third functional group.

From the above consideration, the following model of three-dimensional polycondensation could be formulated. It is assumed that the probability of the third functional group of GHC entering into the reaction is so small that the main reaction is the formation of a linear sequence (*Scheme 1a*).

With excess HMDA molecules (when two of the active functional groups of GHC are already involved in the reaction) these linear sequences react with each other. A reaction occurs between the end groups of HMDA with the third functional group and the GHC branching centre is formed (*Scheme 1b*).

Thus, the formation of a branching centre and, correspondingly, the crosslinking of macromolecules occurs simultaneously with linear polycondensation but at a slower rate. In other words, in the first stage, the polycondensation reaction occurs predominantly with the formation of linear macromolecules with end groups containing bifunctional components. Then, in the second stage, these groups begin to enter into reaction with the third functional group of GHC with the formation of a

Table 3 Influence of the synthesis temperature on the swelling of the gel fraction

Sample no.	Synthesis temperature (°C)	$\mathscr{X}$	W_g	$\bar{M}_{w,o}$ ($\times 10^{-3}$)	Specific amount of absorbed water (g g^{-1})
7	165	1.2	0.4	2.9	0.57
21	200	1.1	0.6	7.2	0.86

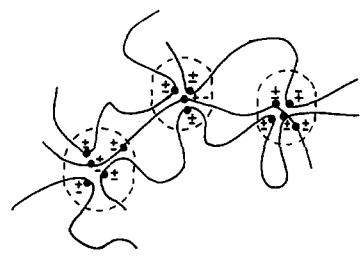

Figure 4 Multiplet structure after the formation of the linear reaction products

branched or crosslinked product. However, it should be emphasized that these stages are not separated in time.

To quantitatively evaluate the degree of polymerization of the initial macromolecules, which we assume to be predominantly linear, the Charlsby theory[13,14] can be applied. This theory was elaborated for the specific process of the crosslinking of macromolecules due to the action of γ-radiation. However, there is no reason to limit the applicability of the quantitative description of the branching process developed in references 13 and 14 only to this mechanism of crosslinking. This theory can be used for the analysis of all the branching or crosslinking processes which take place in the kinetically homogeneous system.

According to Charlsby's classification[13,14], the type of branching given in *Scheme 1b* is called 'end branching': the end of one macromolecule can be connected to any monomer link of another macromolecule with the formation of a branching centre.

In the case when the reaction abilities of the three functional groups of a trifunctional component are not equal (independently of the reasons for this), we can approximately apply the equations which follow from the Charlsby theory[13,14] to the description of three-dimensional polycondensation.

According to references 13 and 14 below the gel point:

$$\bar{M}_w = \bar{M}_{w,o}/(1 - q\bar{M}_{w,o}) \quad (1)$$

$$\bar{M}_n = \bar{M}_{n,o}/[(1 - q\bar{M}_{n,o}/2)] \quad (2)$$

where $\bar{M}_w$ and $\bar{M}_n$ are the weight- and number-average molecular weights of macromolecules, $\bar{M}_{w,o}$ and $\bar{M}_{n,o}$ are the analogous values for the initial linear macromolecules and q is the fraction of links which participate in the formation of branching points. From equations (1) and (2) for the initial most probable *MWD* ($\bar{M}_w/\bar{M}_n = 2$) it follows:

$$\bar{M}_{w,o} = 3\bar{M}_w/[(2\bar{M}_w/\bar{M}_n) - 1] \quad (3)$$

From equation (3) it is possible to estimate $\bar{M}_{w,o}$ if the values of $\bar{M}_w$ and $\bar{M}_n$ are known from experiment. Values of $\bar{M}_{w,o}$ calculated according to equation (3) are given in *Table 1*.

It can be seen that the values of $\bar{M}_{w,o}$ increase with the synthesis temperature. The reason for this is that the increase in the velocity of polycondensation in the first stage of the reaction (*Scheme 1a*) with the increase of temperature is more pronounced than the corresponding increase of the intensity of the crosslinking (second stage of the reaction, *Scheme 1b*).

Another method of estimation of the value of $M_{w,o}$ uses the relations of the Charlsby theory above the gel point. For the given type of branching[13,14]:

$$\bar{M}_{w,o} = 2\frac{M_o}{\mathscr{X}_c - 1} \quad (4)$$

where M_o is the molecular weight of the repeating unit, and $\mathscr{X}_c$ is the value of $\mathscr{X}$ at the gel point (*Figure 2*). The values of $\bar{M}_{w,o}$ calculated according to equation (4) (*Table 1*) are in reasonable agreement with those derived from equation (3). This correlation shows that the Charlsby theory can be used for the characterization of the present process.

Another justification of the applicability of the theory from references 13 and 14 can be seen from *Figure 2*. The solid curves in this figure are plotted according to the theoretical result:

$$W_g = 1 - \{-0.5 + [0.25 + 4/(\mathscr{X} - 1)\bar{M}_{w,o}]^{1/2}\}^2 \quad (5)$$

where the values of $\bar{M}_{w,o}$ were obtained independently from equation (3). It can be seen that the agreement with the experimental data is very good. At the same time, there is no correlation with the Flory theory (curve 4 in *Figure 2*). Therefore, we can conclude that the structure of the branched macromolecules and gels appearing as a result of the present process can be adequately described by the theory proposed by Charlsby[13,14].

The possibility of obtaining mainly linear products in the reaction at some stage in three-dimensional polycondensation is the result of the different velocities of the reactions corresponding to the growth of the linear sequences and to the crosslinking. The networks which are formed in the final stage of this process are analogous to the networks which are obtained in the two stages in the preliminary synthesis of linear polymers with active end functional groups. The advantage of the three-dimensional polycondensation process studied here is that such a polymer network can be obtained in one stage. Moreover, in this case we have the possibility of influencing the crosslinking process and, thus, the network structure by adding small amounts of polar compounds such as water, bases or different salts because the number of ion pairs and multiplets in the networks will strongly depend on the presence of such additives.

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