

Solid-state polyamidation of unsaturated nylon salts: the role of polycondensation water

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Solid-state polyamidation (SSP) processes may proceed under three different modes: in the pure solid state (mode I), through melt intermediates (mode II) and in the pure solid state accompanied by water separation in a different phase (mode III). In previous studies, on typical aliphatic diamine–aliphatic diacid nylon salts, the role of polycondensation water formed has been investigated and a qualitative model has been proposed to explain the typical mode II observed. In this work, monomer structures more organized in terms of polar coordination and rigidity are considered to reveal different modes of SSP behaviour. Ethylenediammonium maleate, ethylenediammonium fumarate and hexamethylenediammonium fumarate were selected to exhibit either coexistence of modes II and III or predominance of mode III. Interpretation of the phenomena in terms of the role of polycondensation water is again attempted.

(Keywords: unsaturated nylon salts; solid-state polycondensation (polyamidation); solid–melt transition; water accumulation)

INTRODUCTION

Solid-state polyamidation (SSP) is widely used in postpolymerizing nylon prepolymers produced in the melt phase^{1–8}. On the other hand, a considerable amount of research work has been accumulated on SSP reactions^{1,9–26} of nylon salts. Oddly enough, such SSP processes—starting from nylon salts—have until now not been used industrially. A possible transition from the solid to the melt state, especially in the very initial stages of the process, seems to comprise one major reason.

In the past the phenomenon of solid–melt transition (SMT) has not been obviously described due to the experimental techniques followed^{2,8,11,12,16–18,26–28} (usually heating of some milligrams of the raw material in a closed chamber under inert atmosphere). Nevertheless, the kinetic data obtained very often fit well typical melt reaction models^{12,16}. Furthermore, considerable indications exist for increased mobility of the reacting species^{8,16,28–30} and also for a distinct change of the prevailing reaction mechanism^{10,12,16,26}.

In previous papers from this laboratory SMT phenomena during SSP runs have been systematically investigated for a variety of aliphatic diamine–aliphatic diacid nylon salts, namely tetra-, hexa- and dodecamethylenediammonium adipate and hexa- and dodecamethylenediammonium sebacate^{19–22,24,25}. All these salts, with different concentration and distribution of hydrophilic groups, when polymerized in the solid state may pass through a melt or quasi-melt stage. The phenomenon has been proved, due to the experimental reaction technique followed.

To explain the solid–melt transition observed, the role of polycondensation water was considered, to reveal, depending however on reaction rate, significant accumulation of this water within the reacting grains^{20,25}. Thus,

on the grounds of the deliquescent behaviour of the salts, it was proposed that water entrapment results in the formation of lower-melting-point areas, overlapping eventually to effect complete breakdown of the reacting crystalline structure. This behaviour has been assigned as mode II, to differentiate from modes I and III, according to which no SMT takes place²⁴. However, in the former case (mode I) diffusion of the by-product formed readily away from the reaction sites is assumed while in mode III some of that is accumulated in a second phase within the reacting structure.

In this paper, in an attempt to increase the 'structural organization' (and therefore resistance to hydration) of the reacting solid³¹, the interest is focused on double-bond-containing monomers of high polar content. High concentration of the polar hydrophilic groups together with the presence of a double bond, especially in the more symmetric *trans* configuration, should contribute to the formation of a well coordinated salt structure responding in a different mode under SSP conditions. Accordingly, ethylene- and hexamethylenediammonium fumarate have been selected for further study²⁴. On the other hand, when changing the configuration of the double bond by the less symmetric *cis* configuration, a considerable decrease of the structural order is expected, and for comparison ethylenediammonium maleate is also considered.

EXPERIMENTAL

Preparation of nylon salts

The procedure already described for the preparation of the dodecamethylenediammonium adipate was followed¹⁹. Experimental results from the stage of salt characterization have been described previously²⁴. It is

Table 1 Solid-state polymerization runs: operational parameters

Grain size	600–700 μm
Ratio salt/inert solvent	20–25 g l^{-1}
Stirring rate	500 rpm
Distillation rate	150 ml h^{-1}
Dispersion agent	Montan wax (2% w/v)

worthwhile to notice that the well organized structures of ethylene- and hexamethylenediammonium fumarate provide no melting point, but only a decomposition point. As expected, this is not the case with ethylenediammonium maleate.

Polymerization

The solid-state polyamidation technique followed, together with a thorough description of the SMT phenomena, have been described in detail previously^{15,19,24,25}. In *Table 1* the values of the operational parameters used are quoted. A grain size in the range between 600 and 700 μm was selected, suitable for microscopy observations. Montan wax (Hoechst Wax S: a mixture of technical-grade montanic acids) was used as a dispersion agent (2% w/v: 2 g of wax per 100 ml of non-solvent employed) to inhibit as much as possible any agglomeration of the reacting grains during 'quasi-solid' or equally 'quasi-melt stages' (QSMS) when softening starts. Obviously, the QSMS phenomenon is a precursor of the solid–melt transition²⁰. On the other hand, to exclude attributing melting behaviour to the particles, because of the presence of the wax, all samples were thoroughly washed with n-hexane to remove wax traces before any microscopic examination.

Characterization

The characterization of the reacting particles was based on end-group analysis, water quantitative determinations and microscopic observations. The exact experimental procedures followed have been described previously^{19,20,24,25}.

RESULTS AND DISCUSSION

Selection of reaction temperature

It has been proved^{9,19,24,25} that any appearance of SMT phenomena is closely related to the difference between the melting point of the nylon salt and the reaction temperature employed. In the extreme case of reaction temperatures very far below the melting point of the salt, SMT is excluded, simply because the rate of solid-state polycondensation is very low¹⁹. For this reason, the salts were tested within a temperature range in which SMT can occur, based on the preliminary experimental findings²⁴. In *Table 2* the temperature levels used for each particular salt are quoted together with the corresponding non-solvent used.

Diffusion parameter (water accumulation factor)

For each polymerization run the following parameters are monitored *versus* reaction time (t)^{20,25}: (a) conversion (p_t) (based on end-group reduction); (b) water content of the reacting mass (w_t); (c) diffusion parameter (D_t).

The diffusion parameter (or water accumulation factor) has been defined in ref. 20 as the fraction of water

accumulated within the reacting grains over the sum of that initially present plus that formed during the polycondensation reaction:

$$D_t = w_t / (w_0 + 11.25p_t c_0)$$

where c_0 represents the weight percentage (% w/w) of amine end-groups in the monomer salt, and w_0 and w_t the water content (in milligrams per gram of the reacting solid) at reaction times 0 and t respectively.

Solid-state polyamidation runs: ethylenediammonium maleate

Ethylenediammonium maleate/n-octane. In *Figure 1* data for the system ethylenediammonium maleate/n-octane are presented. The following observations can be made.

Data of p_t vs. t (*Figure 1*, curve A) show an induction period, lasting for 2 h, after which the appearance of a quasi-melt stage is evident (*Figure 2*). This stage is of about 1 h duration and then the reacting grains harden again. It should be mentioned that after the solid-state character of the process is restored, the reaction is not further studied because it turns into a typical solid-state postpolymerization process of the oligomer formed¹⁹, a subject extensively studied already^{1–8}.

Turning to water aspects, *Figure 1* (curve B) shows that during the induction period the water accumulated increases considerably with reaction time up to the quasi-melt or quasi-solid stage. Then the reaction rate increases, but more by-product can escape from the reacting grains (*Figure 1*, curve C). It is again proposed that the QSMS phenomenon appears because of the hydration mechanism already discussed for the aliphatic

Table 2 Reaction temperatures selected

Nylon salt	Reaction temperature (°C)	Liquid employed
Ethylenediammonium maleate (m.p. 161°C)	126	n-Octane
	138	p-Xylene
Ethylenediammonium fumarate (d.p. 202°C)	151	n-Nonane
	174	n-Decane
Hexamethylenediammonium fumarate (d.p. 212°C)	174	n-Decane
	195	n-Undecane

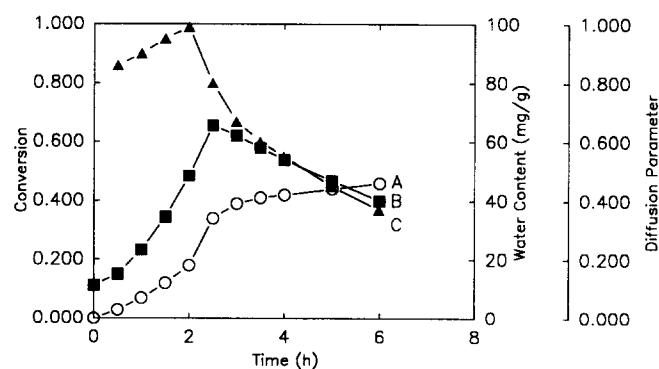


Figure 1 Ethylenediammonium maleate: plots of conversion p (○, curve A), of the water content of the reacting mass w_t (■, curve B) and of the diffusion parameter D_t (▲, curve C) *versus* time at 126°C (b.p. of n-octane)

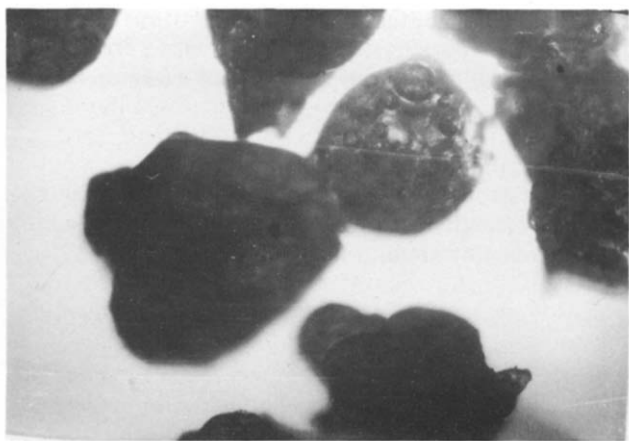


Figure 2 Reacted crystals of ethylenediammonium maleate after 2 h at 126°C ($\times 65$)

diamine–aliphatic diacid nylon salts^{20,25}. Nevertheless, what is new is concerned with the separation of some of the water in a second phase. This becomes evident by the presence of bubbles and blisters in the reacting structure (Figure 2) and therefore coexistence of modes II and III is now observed.

It is worth while mentioning that the appearance of the separate by-product phase became microscopically evident only after 1 h reaction time. This means that the comparatively rich in polar content and better organized structure of ethylenediammonium maleate initially can accommodate some of the water produced. Nevertheless, above one level and at the given reaction rate it seems that the excess water molecules formed cannot be sorbed locally, but also cannot diffuse away either out of the reacting grains or to other ‘empty’ polar sites. On the other hand, no severe disturbance and breakdown of the reacting structure readily takes place due to the good organization of the latter. Accordingly, any disorganized areas of the solid may serve as accommodating areas for this excess water, i.e. as nucleating sites for the development of the second phase²⁴. Of course, at higher reaction rates a complete breakdown is not excluded.

Ethylenediammonium maleate/p-xylene. In Figure 3 the behaviour of this salt is shown at the boiling point of *p*-xylene (138°C). In agreement with the behaviour of the aliphatic diamine–aliphatic diacid nylon salts under similar conditions^{19,24,25}, the reaction from the very beginning is characterized by a distinct transition to the melt state. This is the case independently of the presence of dispersion agent. The melt stage lasts for 1.5 h and afterwards the reacting mass solidifies again. On the other hand, during the initial melt stage and in spite of the increased reaction rate, an extended water accumulation is not observed due to the mobility conditions in the reacting system²⁰. Nevertheless, the difference from the aliphatic salts is concerned with the considerably higher water contents accumulated now. Also there is microscopic evidence for the development of a separate water phase from the very beginning of the reaction. The bubbles or blisters formed increase in magnitude, and after the mass resolidifies, they start breaking. This coincides with the maxima of the curves B and C in Figure 3.

The above picture indicates that for higher reaction rates the same qualitative model applies but, due to the

significantly higher rates of water formation, there is no time for an organized arrangement of the water molecules formed at the polar hydrophilic groups. As a result, the crystalline structure is now from the beginning very severely disturbed but also with some water entrapment in a second phase.

The complexity of the total reaction course, in agreement with previous investigators^{12,16,26}, is also reflected by kinetic studies. At both temperature levels examined none of the 11 kinetic models considered¹⁹ fit satisfactorily the conversion (p , vs. t) data. On the contrary, for mode II behaviour^{19,20,25} and low reaction rates, the model of nucleation and growth predominates. At higher rates, second-order kinetics in the melt stage are followed by a solid-state stage where three-dimensional diffusion controls.

Solid-state polyamidation runs: ethylene- and hexamethylenediammonium fumarate

When shifting to the salts of ethylene- or hexamethylenediamine with fumaric acid the above observed coexistence of modes II and III may not always be the case.

Ethylenediammonium fumarate/n-nonane, n-decane. In Figure 4 data are presented for reacting ethylenediammonium fumarate at the boiling point of the *n*-nonane (151°C). Based on both macroscopic and microscopic observations it was found that the reaction proceeds

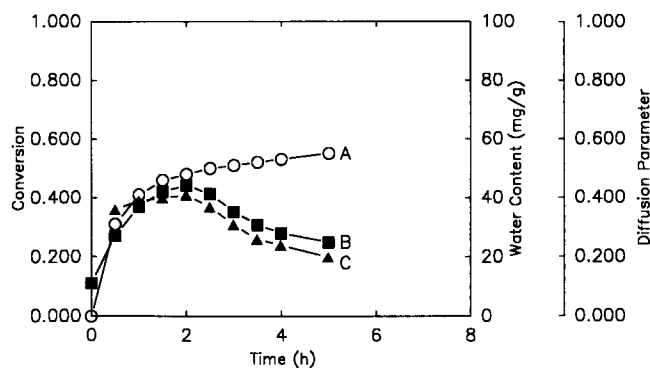


Figure 3 Ethylenediammonium maleate: plots of conversion p (○, curve A), of the water content of the reacting mass w_t (■, curve B) and of the diffusion parameter D_t (▲, curve C) versus time at 138°C (b.p. of *p*-xylene)

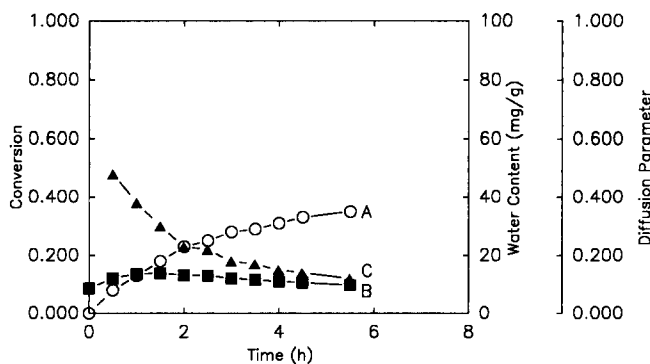


Figure 4 Ethylenediammonium fumarate: plots of conversion p (○, curve A), of the water content of the reacting mass w_t (■, curve B) and of the diffusion parameter D_t (▲, curve C) versus time at 151°C (b.p. of *n*-nonane)

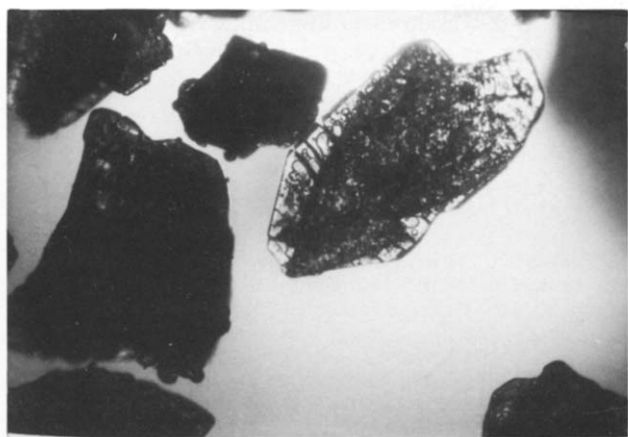


Figure 5 Reacted crystals of ethylenediammonium fumarate after 1.5 h at 151°C ($\times 65$)

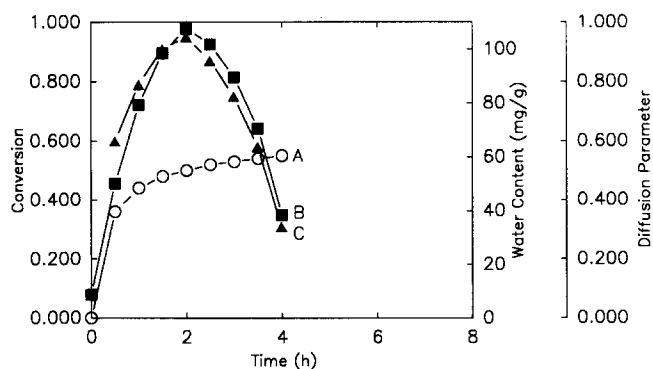


Figure 6 Ethylenediammonium fumarate: plots of conversion p (○, curve A), of the water content of the reacting mass w_t (■, curve B) and of the diffusion parameter D_t (▲, curve C) versus time at 174°C (b.p. of *n*-decane)

continuously in the solid state. Nevertheless, from the very beginning, the presence of the separate water phase is evident (Figure 5).

The aforementioned observations are in agreement with Figure 4 (curve C) in which considerable water accumulation is revealed at the beginning of the process. Nevertheless, this accumulation is continuously decreasing with time together with the reaction rate (Figure 4, curve A). On the other hand, the conversion data obey well typical diffusion models¹⁹.

Based on the above picture it can be said that indeed the ethylenediammonium fumarate due to its perfectly organized structure provides a limiting behaviour. The polycondensation water (especially in the inner parts of the reacting crystal), after possibly some hydration of the nearest hydrophilic groups, has two options: either diffusion out of the reacting grain or diffusion to disorganized areas and separation in a second phase. In both cases, severe disturbance of the crystalline structure to clustering or formation of highly hydrated areas (SMT or QSMS phenomena) is now not favoured due to the high 'quality' of the reacting structure.

The aforementioned suppositions are consistent with the picture obtained from the SSP run of the same salt at the boiling point of *n*-decane (174°C) (Figure 6). In spite of the high reaction rate the process proceeds continuously in the solid state while separation of water in a second phase occurs to a great extent from the very beginning (Figure 7). The by-product accumulation takes

high values (Figure 6, curves B and C), but no transition phenomena are observed. After 2 h most of the blisters start breaking and the water entrapped is released, leading to the decreasing trend of D_t . On the other hand, none of the kinetic models considered satisfactorily fit the conversion data.

It is worthwhile mentioning again here that the stability of ethylenediammonium fumarate against transition behaviour has been proved²⁴, even at 195°C, i.e. only 7°C below its decomposition point.

Hexamethylenediammonium fumarate/n-decane, n-undecane. Hexamethylenediammonium fumarate comprises an interesting case, since its structure resembles that of ethylenediammonium fumarate, but its polar content is considerably lower, with the result that one expects less intensive organization. The experimental data obtained are consistent with the qualitative model proposed.

At the boiling point of *n*-decane the reaction proceeds very slowly in the solid state so that after 12.5 h the conversion obtained did not exceed the level of 3%. On the contrary, at the boiling point of *n*-undecane an interesting behaviour was monitored. The data obtained are presented in Figure 8. As expected, the hexamethylenediammonium fumarate fails to match pure mode III behaviour, especially at this very high temperature. After reacting for about 3 h the reacting

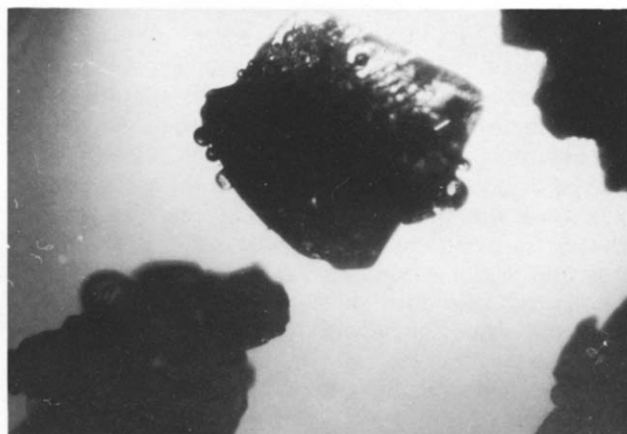


Figure 7 Reacted crystals of ethylenediammonium fumarate after 1 h at 174°C ($\times 65$)

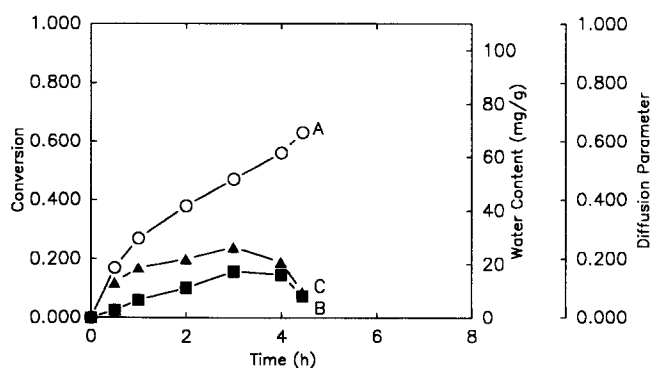


Figure 8 Hexamethylenediammonium fumarate: plots of conversion p (○, curve A), of the water content of the reacting mass w_t (■, curve B) and of the diffusion parameter D_t (▲, curve C) versus time at 195°C (b.p. of *n*-undecane)

crystals started losing their distinct and sharp edges due to the appearance of a less evident quasi-melt stage. This lasts up to the end of the reaction and it seems to be accompanied by some increase of the reaction rate and by reduction of the water accumulation factor. On the other hand, separation of water in a second phase was not detected from the beginning, but again after about 3 h. Furthermore, fitting of the p_t vs. t data to all kinetic models was poor.

From the point of view of water it seems that most of that formed escapes easier out of the reacting crystals so that no significant accumulation is observed (Figure 8, curve C). Nevertheless, the remaining increases with time up to the appearance of the quasi-solid stage and water phase separation. This behaviour initially resembles more that of the system hexamethylenediammonium maleate/*n*-octane where, however, the difference between the melting point of the salt and the reaction temperature is 35°C. For the same salt, when this difference comes to the level of 23°C (non-solvent: *p*-xylene) transition to the melt stage is readily observed. On the contrary, in the present system, with a temperature difference of 17°C no SMT is detected, but in spite of lower water accumulation QSMS phenomena and water separation in a second phase eventually appear. Under these considerations, hexamethylenediammonium fumarate presents rather an intermediate behaviour between ethylenediammonium maleate and ethylenediammonium fumarate, and this seemed to be a good guess based on structural characteristics.

CONCLUSIONS

Solid-state polyamidation processes comprise very complicated reactions due to the variety of phenomena that may take place. Different modes of SSP behaviour seem to be correlated with the role of the water formed in terms of the 'organization' of the reacting monomer structure. Accordingly, in nylon salts of moderate structural organization the model of water accumulation-hydration-transition to the melt state predominates, while when the network of the coordinating polar groups becomes more rigid deviation from this model may occur. Water accumulation does not necessarily lead to hydration, but also to phase separation. The phenomena are competitive, coexistence of different modes can take place, and in extreme cases of structural organization any SMT or QSMS phenomena are excluded. Accordingly, what seems feasible within the limits of this investigation is that when knowing the structural characteristics of the starting monomer one

may predict the mode encountered in next SSP runs. The latter point may be the eventual gain of this research.

REFERENCES

- 1 Flory, P. G. (E. I. du Pont de Nemours and Co.) US Pat. 2 172 374, 1939
- 2 Bruck, S. D. *Ind. Eng. Chem., Prod. Res. Dev.* 1963, **2** (2), 119
- 3 Chen, F. C., Griskey, R. G. and Beyer, G. H. *AIChE J.* 1969, **15** (5), 680
- 4 Beaton, D. H. (E. I. du Pont de Nemours and Co.) Ger. Offen. 2 232 304, 1973
- 5 Endo, T., Ihata, J. and Fujimoto, A. (Asahi Chemical Industry Co. Ltd), Japan Pat. 73 23 199, 1973
- 6 Shigemura, S. and Yamada, M. (Toray Industries Inc.), Japan Pat. 76 27 719, 1976
- 7 Kobayashi, T., Takano, M., Yamada, M. and Yokoyama, T. (Toray Industries Inc.), Japan Kokai 74 98 496, 1974
- 8 Gaymans, R. J. and Schuijjer, J. in 'Polymerization Reactors and Processes' (Eds. J. N. Henderson and T. C. Bouton), *Am. Chem. Soc. Symp. Ser.* 1979, **104**, 137
- 9 Volokhina, A. V., Kudryavtsev, G. I., Skuratov, S. M. and Bonetskaya, A. K. *J. Polym. Sci.* 1961, **53**, 289
- 10 Oya, S., Tomioka, M. and Asaki, T. *Kobunshi Kagaku* 1966, **23** (254), 415
- 11 Macchi, E. M., Morosoff, N. and Morawetz, H. *J. Polym. Sci. (A-1)* 1968, **6**, 2033
- 12 Khripkov, E. G., Kharitonov, V. M. and Kudryavtsev, G. I. *Khim. Volokna* 1970, **6**, 615
- 13 Khripkov, E. G., Kiya-Oglu, V. N., Kharitonov, V. M. and Kudryavtsev, G. I. *Vysokomol. Soedin (B)* 1972, **14** (3), 189
- 14 Khripkov, E. G., Lavrov, B. B., Kharitonov, V. M. and Kudryavtsev, G. I. *Vysokomol. Soedin (B)* 1976, **18** (2), 82
- 15 Kampouris, E. M. *Polymer* 1976, **17**, 409
- 16 Dasgupta, P. Ph.D. Thesis, University of Akron, 1978
- 17 Volokhina, A. V., Kudryavtsev, G. I., Raeva, M. V., Bogdanov, M. N., Kalmykova, V. D., Mandrosova, F. M. and Okromchedlidze, N. P. *Khim. Volokna* 1964, **6**, 30
- 18 Monroe, G. C. (E. I. du Pont de Nemours and Co.) US Patent 3 031 433, 1962
- 19 Papaspyrides, C. D. and Kampouris, E. M. *Polymer* 1984, **25**, 791
- 20 Kampouris, E. M. and Papaspyrides, C. D. *Polymer* 1985, **26**, 413
- 21 Papaspyrides, C. D. and Kampouris, E. M. *Polymer* 1986, **27**, 1433
- 22 Papaspyrides, C. D. and Kampouris, E. M. *Polymer* 1986, **27**, 1437
- 23 Papaspyrides, C. D. *J. Polym. Sci. (C)* 1987, **25**, 363
- 24 Papaspyrides, C. D. *Polymer* 1988, **29**, 114
- 25 Papaspyrides, C. D. *Polymer* 1990, **31**, 490
- 26 Frayer, P. D. and Lando, J. B. *Mol. Cryst. Liq. Cryst.* 1969, **9**, 465
- 27 Griskey, R. G. and Lee, B. I. *J. Appl. Polym. Sci.* 1966, **10**, 105
- 28 Gaymans, R. J., Amirtharaj, J. and Kamp, H. *J. Appl. Polym. Sci.* 1982, **27**, 2513
- 29 Zimmerman, J. *J. Polym. Sci., Polym. Lett. Edn.* 1964, **2**, 955
- 30 Bagramyants, B. A., Volokhina, A. V., Kudryavtsev, G. I. and Enikolopyan, N. S. *Vysokomol. Soedin. (A)* 1967, **9** (1), 183
- 31 Rubin, J. *J. Polym. Sci., Polym. Lett. Edn.* 1967, **5**, 1135