The production of polyimide foam materials based on acrylonitrile and (meth)acrylic acid

P.V. Kornienko,1 K.V. Shirshin,1,2 Yu.P. Gorelov,1 A.V. Kuznetsova,1 G.N. Chervyakova,1 and T.A. Khokhlova1

1V.A. Kargin Polymer Chemistry and Technology Scientific Research Institute, with Experimental Works, Dzerzhinsk, Nizhny Novgorod
2Dzerzhinsk Polytechnic Institute (Branch), R.E. Alekseev State Technical University, Nizhny Novgorod

SUMMARY

A study was made of the influence of the structure and ratio of the principal monomers, and also the microstructure of obtained block copolymers of (meth)acrylonitrile and (meth)acrylic acid, on the formation, in the process of heat treatment, of poly(meth)acrylimide foam materials.

In the development of modern planes, trains, automobiles, and boats, increasingly wide use is being made of multilayer load-bearing elements consisting of thin outer layers of glass- or carbon-fibre-reinforced plastic and a thick inner layer of light filler. The use of such designs makes it possible to lower considerably the weight of parts while retaining high strength characteristics. Among the promising polymer fillers are polymethacrylimide (PMI) plastic foams [1]. Through the formation, in the process of heat treatment of the copolymers, of glutarimide rings, the given foam materials possess high heat resistance and strength. A two-stage industrial scheme has now been implemented abroad for the production of such plastic foams. At the first stage, by bulk polymerisation, copolymers of methacrylonitrile (MAN) and methacrylic acid (MAA) are produced (reaction 1), which at the second stage are heat treated, with the production of PMI foam (reaction 2). It must be noted that PMI plastic foams produced by the given technology have a fairly high cost, which is due in large part to the use of scarce and expensive MAN in the process.

At present, there is no information on the industrial production of foam materials based on multitonnage acrylonitrile (AN), acrylic acid (AA), or MAA. In a number of studies it has been shown that PMI foam materials based on readily available AN and MAA possess physicomехanical properties that are not inferior to those of foam materials based on MAN–MAA copolymers [2–4]. However, the indicated studies focus on the second stage of the process, i.e. the imidisation and foaming of block copolymers, while the laws governing the first stage, i.e. the bulk copolymerisation of nitrile and acid, have as yet not been presented in the literature.

Therefore, in this work, an examination was made of the features of the bulk copolymerisation of AN with (M)AA with the aim of assessing the possibility of the subsequent production of PMI foam materials based on the copolymers.

From the imidisation reaction scheme given above it can be seen that the microstructure of the initial copolymer should have a considerable influence on the concentration of glutarimide units formed in the polymer chain. Ideally, to achieve the maximum content of imide units in the...
plastic foam, strict alternation of nitrile and carboxyl groups should be observed in the initial copolymer. In this connection, the question of the relative activities of the monomers becomes important.

**EXPERIMENTAL**

Before use, the MAN, AN, MAA, and AA were purified by distillation. Perkadox 16 and TBS were used without additional purification.

The production of foam material was carried out in two stages. At the first stage, by block polymerisation in moulds of silicate glass in the presence of 0.2% initiator di-[4-tert-butylcyclohexyl]peroxydicarbonate (Perkadox-16; AkzoNobel) at 30°C, (M)AN–(M)AA copolymers of different composition were produced. After 20 h, the temperature was raised gradually to 100°C and held for 1 h. The monomer conversion in all experiments amounted to at least 99.5%. The blowing agent (TBS) in a quantity of 5% was introduced into the reaction mixture at the stage of copolymer synthesis. At the second stage, copolymer specimens were subjected to foaming at 200°C without limitation of volume for 1 h.

The individual concentrations of AN and MAA were estimated by gas–liquid chromatography. Gas–liquid chromatography was carried out on a Chrom-5 instrument with a flame ionisation detector and a glass column of 2.5 m length and 3 mm diameter, filled with sorbent: 8% polyethylene glycol adipinate + 2% H₃PO₄ on Chromosorb® W; the gas carrier (helium) flow rate was 40 mL/min; the evaporator temperature was 210°C; the column thermostat temperature was 150°C.

The density of the heat-treated copolymers was determined on 100 x 100 x 10 mm specimens in accordance with the GOST 409-77 standard. Strength tests of plastic foam specimens were conducted on a Testometric M350-AT tensile testing machine (force measurement 100 MPa) in accordance with GOST 23206-78. Micrographs of the plastic foam were obtained on a Hitachi-S2500 electron scanning microscope. The degree of swelling of the AN–AA copolymer was determined from the increase in weight of specimens weighing 0.1 g after holding in DMF at 20 ± 2°C. IR spectra of the heat-treated copolymers were taken on an IR Affinity-1 Fourier spectrometer. Specimens were prepared in the form of pellets pressed with potassium bromide.

The data presented in Table 1 indicate that, in all the examined monomer pairs, the acid is more active than the nitrile. Here, the ratio of \( r_2 \) to \( r_1 \) for the various monomer pairs is not identical and varies from 2.7 (for the MAN–MAA pair) to 41 (for AN–MAA). Consequently, a copolymer based on AN and MAA should possess greater compositional inhomogeneity by comparison with other monomer pairs: at low conversions, the copolymer should be appreciably rich in acid units, and at high conversion in nitrile units. This is confirmed by experimental data, from which it can be seen that, in the process of polymerisation, MAA is consumed much more rapidly than AN (see Figure 1). During the copolymerisation of AN with MAA, with an equimolar monomer ratio, it was noted that, at a conversion of over 15–20%, a copolymer was formed from the monomer blend, and then the process proceeded under heterogeneous conditions with the formation of an opaque, white block (Figure 2c). The copolymerisation of MAN with MAA and of AN with AA at low conversions also proceeded under conditions of limited solubility of the copolymers in the monomer blend. However, when high conversions (over 60%) were reached, the reaction mixtures again became homogeneous (Figures 2a and b).

Taking into account the large difference in values of the coefficients of relative activities of the monomers used in the work (see Table 1), it is logical to assume

![Figure 1. The change in the concentration of AN (1) and MAA (2) during their copolymerisation](image)

![Figure 2. Specimens of copolymers MAN–MAA (a), AN–AA (b), and AN–MAA (c). [(M)AN]:[(M)AA] = 5:5](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>(M)AN</th>
<th>(M)AA</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_2/r_1 )</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MAN</td>
<td>MAA</td>
<td>0.59</td>
<td>1.63</td>
<td>2.76</td>
<td>[5]</td>
</tr>
<tr>
<td>2</td>
<td>AN</td>
<td>AA</td>
<td>0.62</td>
<td>1.64</td>
<td>2.65</td>
<td>[6]</td>
</tr>
<tr>
<td>3</td>
<td>AN</td>
<td>MAA</td>
<td>0.35</td>
<td>1.15</td>
<td>3.29</td>
<td>[7]</td>
</tr>
<tr>
<td>4</td>
<td>AN</td>
<td>MAA</td>
<td>0.13</td>
<td>5.37</td>
<td>41.31</td>
<td>[2]</td>
</tr>
<tr>
<td>5</td>
<td>AN</td>
<td>MAA</td>
<td>0.15</td>
<td>5.50</td>
<td>36.67</td>
<td>[8]</td>
</tr>
</tbody>
</table>
that the properties of the PMI foam materials produced by the heat treatment of copolymers based on AN and MAA will differ appreciably from PMIs synthesised on the basis of AN–AA and MAN–MAA copolymers. The low values of the bulk copolymerisation constants that were obtained for the MAN–MAA and AN–AA pairs give grounds for assuming the similarity of the microstructure of these copolymers and consequently the similarity of the physicomechanical properties of PMI based on them.

However, as shown by experimental data, after the heat treatment of AN–MAA and AN–AA produced by the polymerisation of equimolar monomer blends, the formation of foam products was not observed (Figures 3b and c; Table 2, Nos 3 and 4). Specimens of copolymers based on MAN–MAA, produced under similar conditions, were foamed isotropically with increase in the linear dimensions roughly by a factor of 2 and with the formation of a rigid closed-cell structure (Figure 3a; Table 2, No. 1).

One of the main reasons for this difference in behaviour of copolymers during heat treatment may be features of their microstructure, on which depend both the direction and the extent of chemical transformations with the participation of acid and nitrile groups. Some features of the composition of the copolymers produced in the work were assessed by IR spectroscopy.

It is well known [2, 6] that, during the heat treatment of copolymers based on (M)AN–(M)AA, depending on the arrangement of the acid and nitrile units in the polymer chains, processes of imidisation (reaction 2), the formation of anhydride units (reaction 3), and cyclisation of the nitrile groups (reaction 4) may occur:

In the IR spectra of products of these reactions, pronounced C–N–C signals of the imide group (1210–1220 cm\(^{-1}\)) should be present, a signal at 1020 cm\(^{-1}\) associated with deformation vibrations of the C–O–C group, two signals at 1750 and 1850 cm\(^{-1}\) relating to vibrations of the –C=O groups of the anhydride [2], and also a broad multiplet signal in the 1490–1690 cm\(^{-1}\) region corresponding to the C=N–C group of the conjugated polycyclic structure (reaction 4) [6].
differs. For example, in the spectrum of the AN–MAA copolymer, all three signals of the anhydride groups (1020, 1750, and 1850 cm$^{-1}$) are pronounced, in the MAN–MAA copolymer the given signals appear only in the form of a shoulder at 1850 cm$^{-1}$ and a weak peak at 1020 cm$^{-1}$, and on the spectrum of the AN–AA copolymer they are absent altogether.

![Figure 4. IR spectra of heat-treated copolymers MAN–MAA (1), AN–MAA (2), and AN–AA (3). In the initial copolymers, [(M)AN]$_0$:[(M)AA]$_0$ = 5:5](image)

The presence in the IR spectrum of the heat-treated AN–MAA copolymer of intense signals of the anhydride units and a less pronounced signal of the imide group is confirmation of the above assumption concerning the high compositional inhomogeneity and consequently the presence of a considerable number of block fragments of the initial copolymer.

It is interesting that the copolymer based on AN and AA did not foam in the process of heat treatment, although imidisation reactions occurred [the IR spectra in Figure 4 (1, 3) of the heat-treated AN–AA and MAN–MAA copolymers are fairly similar]. This may be due to a known feature of the bulk polymerisation of acrylic monomers – the crosslinking of the macromolecules by the occurrence of chain transfer reactions to the polymer. The formation of a crosslinked structure of the AN–AA copolymer is confirmed by data on the solubility of the copolymers in polar solvents – dimethylsulphoxide, dimethylformamide, and dimethylacetamide. Thus, MAN–MAA and AN–MAA copolymers possess good solubility in the given solvents, while the copolymer based on acrylic monomers swells only slightly in these solvents. The time dependence of the degree of swelling of the AN–AA copolymer in dimethylformamide is presented in Figure 5.

Thus, during the heat treatment of [(M)AN]–[(M)AA] copolymers produced by the polymerisation of equimolar monomer blends, foamability was possessed only by copolymers based on methacrylic monomers. Limited foaming of the copolymer based on AN–MAA seems to be associated with features of the microstructure of the polymer molecules [a significant microblock nature], while foaming of the copolymer based on acrylic monomers is prevented by crosslinking of the macromolecules. Here, as can be seen from the IR spectra presented in Figure 4, the concentration of imide groups after heat treatment of copolymers based on AN and AA is similar to that for PMIs produced on the basis of MAN and MAA. Therefore, if the foamability of the polymeric material is not a key problem, then, on the basis of AA–AN block copolymers, interesting heat-resistant materials can be produced.

The main task in the production of PMIs based on AN and MAA is the synthesis of copolymers of more homogeneous microstructure. One of the methods for lowering the microblock nature of the copolymers is to increase the concentration of low-activity monomer in the initial reaction mixture. Study of the influence of the ratio of AN and MAA on the progress of bulk polymerisation showed that change in the relative concentration of nitrile in the copolymer from 50 to 60 mol% and above leads to the production of transparent polymer blocks with an intense yellow-brown colour. Comparison of the IR spectra of heat-treated AN–MAA copolymers of different composition [Figure 4 (2) and Figure 6 (1–3)] showed that increase in the proportion of nitrile in the
initial monomer blend to 60 mol% leads to a marked reduction in intensity of the anhydride signals [Figure 6 (1)]. Further increase in the proportion of AN in the reaction mixture leads to the total disappearance of these signals in the spectrum of the heat-treated copolymer. It is important to note that copolymers produced in excess AN foamed fairly well. However, as can be seen from Figure 3 and Table 2 (No. 3), the structure and properties of the obtained plastic foam based on a 6:4 AN:MAA copolymer differ considerably from the corresponding parameters of PMIs produced from methacrylic monomers (see Figures 3d to f and Table 2). It can be seen that, with increase in the proportion of AN in the copolymer, the density and compressive strength of the obtained foam materials increases, whereas for the MAN–MAA copolymer an increase in the proportion of nitrile leads to a reduction in these properties (Table 2). The structure of the obtained plastic foams also differs appreciably. For example, the cell size of the heat-treated 6:4 AN:MAA copolymer is 8–15 times smaller than that of PMIs based on a MAN–MAA copolymer of similar composition. On the whole, with increase in the proportion of nitrile in the AN–MAA copolymer, the cell size of the plastic foam and also the linear expansion of the copolymer specimens decrease (Table 2, Nos 3 to 5; Figures 3e and f), and with an AN concentration in the monomer blend of over 80 mol% the copolymer loses its foamability. This may be due to an increase in the content of rigid conjugated polycyclic structures in the copolymer, which is confirmed by change in the signals in the IR spectrum in the region 1500–1650 cm$^{-1}$ (Figure 6c). The increase in the concentration of nitrile rings in the copolymer explains the intense brown colour of the copolymers produced in excess nitrile.

Thus, it was shown that the production of PMI foams based on AN–MAA block copolymers is possible only with excess nitrile in the initial monomer blend. The formation of PMI foams based on AN and AA is prevented by the crosslinking of the initial copolymer.

REFERENCES
