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Polymers of Acrylonitrile and the Naphthalimide Derivatives of some Fluorescent Dyes

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ABSTRACT

Coloured polymers of acrylonitrile with 4 polymerizable fluorescent dyes (1,8-naphthalimide derivatives) have been obtained. The influence of the dye on thermostability and the molecular weights of the coloured polymers have been determined. It was established that between 85 and 95% of the dye was incorporated into the polymer molecule, providing resistance to wet treatments and solvents. © 1997 Elsevier Science Ltd

INTRODUCTION

The co-polymerization of the traditional monomers with polymerizable dyes is a method for obtaining so called 'self-coloured' polymers. It is also a very interesting route to the subtle modification of polymers. By co-polymerization with appropriate compounds, polymers with desired properties such as fluorescence, photo- and thermostability, solubility or biological activity can be obtained.

We have earlier reported the synthesis of some polymerizable azo-anthraquinonic and benzanthronic dyes which are able to co-polymerize with styrene, acrylonitrile and methyl methacrylate. We have also investigated the influence of the product on the polymerization process as well as the properties of the polymers thus obtained [1–3].

Among the various classical luminophores, derivatives of naphthalimide have been successfully applied in the mass coloration of polymers as markers in biomaterials and so on [4]. Some polymerizable *N*-allylnaphthalimide dyes have also been synthesized and evaluated for their photochemical properties and their ability to co-polymerize with styrene [5,6].

Polymers and co-polymers of acrylonitrile (AN) are widely applied in industry. It was felt to be of interest to investigate the possibility for obtaining polymers of AN with the aforementioned dyes and to establish their influence on some of the co-polymer properties.

EXPERIMENTAL

Materials

Naphthalimide derivatives were obtained by methods described previously [5,6]. AN was purified by redestillation under vacuum under a N_2 atmosphere. DMF, CH_3OH, CH_2Cl_2 and azobisisobutironitrile (ABIN) were of analytical grade.

Analysis

Investigations of the thermal stability of the dyes and of the polymers were performed on a Dupont 2000 DSC unit in an athmosphere of nitrogen in the interval between 20 and 500°C for dyes and 20–300°C for polymers.

Spectrophotometric investigations were made on a Kontron UVICON 860 spectrophotometer in DMF solutions $1\times10^{-4}\,g/cm^3$ for the dyes and $3\times10^{-3}\,g/cm^3$ for the intrinsically coloured polymers.

Investigations of some of the structural features of the dyes were performed on a scanning electron microscope, Jeol 2000/EDX.

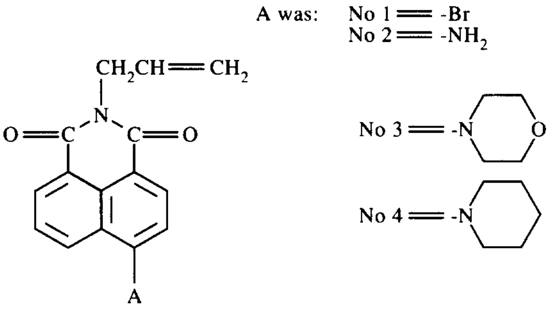
Viscometric investigations of the polymers, involving determination of the $[\eta]$, were made on an Ubbelode viscometer at 30°C. The polymer solutions had initial concentrations of $0.02\,g/cm^3$ in DMF. On the basis of the obtained data, $\alpha=0.72$ and $k=33.5\times10^{-3}$, viscosity average molecular weights were calculated [7].

Polymerization

20 g AN, 1 g ABIN and 0.2 g of the corresponding dye were dissolved in $80\,cm^3$ of DMF. Each flask was flushed with dry, pure nitrogen and heated at 70°C. After 3 h, the mixture was poured into water. The polymer thus isolated was purified from unreacted monomers by 24 h extraction with CH_2Cl_2 and then dried under vacuum, at 50°C, to constant weight.

RESULTS AND DISCUSSION

The polymerization of AN in the presence of the 4 dyes with general formula I was investigated.



(I)

Investigation of the thermal stability of the dyes

Prior to investigation of the polymerization behaviour of the dyes, it was considered to be of interest to study their thermal stability. These studies were performed under stationary conditions in a nitrogen athmosphere in the temperature range 20–500°C. From the data presented in Figs 1–4, we can see that dye **1a** was stable to 280°C. Dye **2** had two points for melting, indicating the possibility of two crystal modifications. Thermal decomposition for the first and second modifications began at 242 and 362°C, respectively. Dye **3** was stable to 123°C and dye **4** began to decompose at temperatures beyond 330°C.

On the basis of these data the thermostability of the dyes is in the order: $4 > 1 > 2 > 3$.

Our conclusion was that all dyes would be stable enough to withstand the thermal exposure arising during copolymerization with AN.

Investigation of the structural features of the dyes

The structure of monomeric dyes is of importance to their compatibility and solubility during co-polymerization. Thus, it was of interest to study the nature of the monomeric dyes. The data received by electronic microscopy, are shown in Figs 5–8. It was established that only dye **1** was largely amorphous. The others had various degrees of organization.

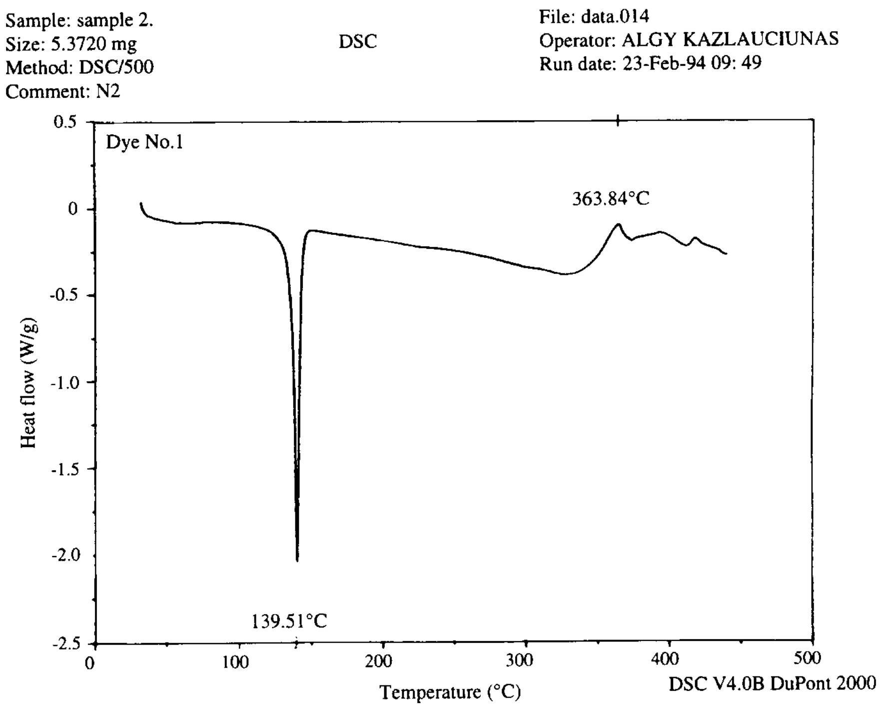


Fig. 1. DSC profile for the bromo form of the allyl chromophore (**I**).

Polymerization of AN with the monomeric dyes

On the basis of preliminary experiments, the most suitable conditions for polymerization were established: temperature 70°C, 5% of the initiator (ABIN) and 1% of the corresponding dye. The polymerization was carried out in solution in DMF (20% (vol.) of monomers) for 3 h. The coloured polymers were isolated in good yield (70–80%) by precipitation in water. After 24 h extraction with CH_2Cl_2 to remove the unreacted monomers, the polymers retained their colour and intense fluorescence. This gives an indication of the covalent bonding of the dye in the polymer molecule. The polymers thus purified were dried under vacuum, at 50°C, to constant weight and subsequently analysed.

Spectrophotometrical investigation

UV/Vis spectra for the polymers were recorded and compared to those of the corresponding monomeric dyes. There was neither a hypsochromic nor bathochromic shift in the absorption spectra observed. Therefore, by the method of the standard calibration curve, the percentage of the reacted (chemically bonded) dye in the polymer was calculated. The data obtained are presented in Table 1. Considering that, during the extraction, a part of the reacted dye could be removed in the low-molecular weight fraction, this percentage value for dyes **1**, **2** and **4** is satisfactory. However, for dye **3**, the percentage of reacted dye was only 51%.

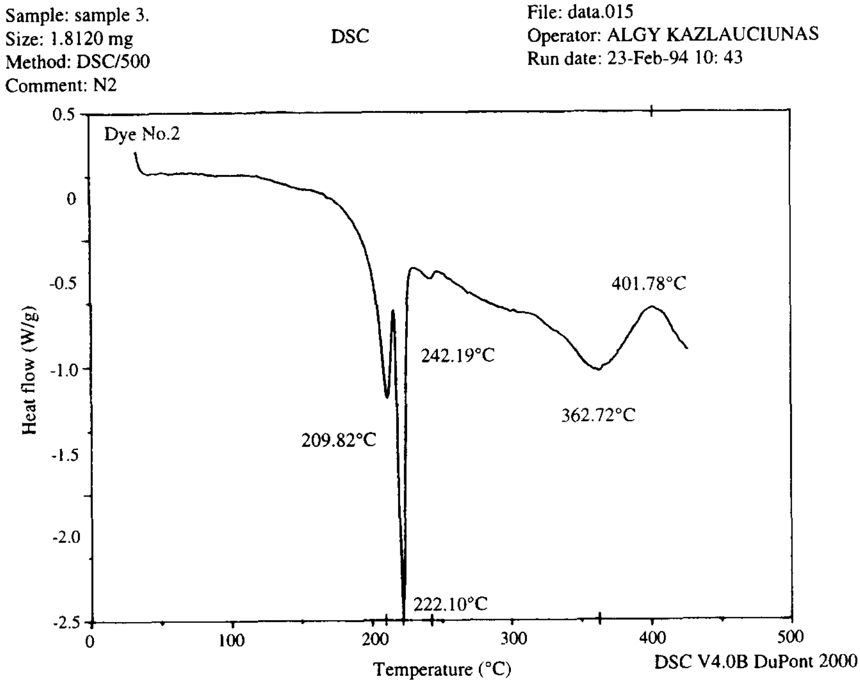


Fig. 2. DSC profile for the amino form of the allyl chromophore (**I**).

TABLE 1
Polymeric Chromophore–Co–Acrylonitrile Characteristics

Dye no.	Chemically bonded dye (%)	$[\eta]$ cm^3/g	Molecular weight[a] g/mol	Initial thermal degradation onset temperature °C
1	85	0.280	11 700	279
2	95	0.180	6200	265
3	51	0.168	5600	275
4	90	0.225	8500	268
Without dye	-	0.342		261

[a] $\alpha = 0.72$, $k = 33.5 \times 10^{-3}$ cm^3/g (Mark Honwich parameter).

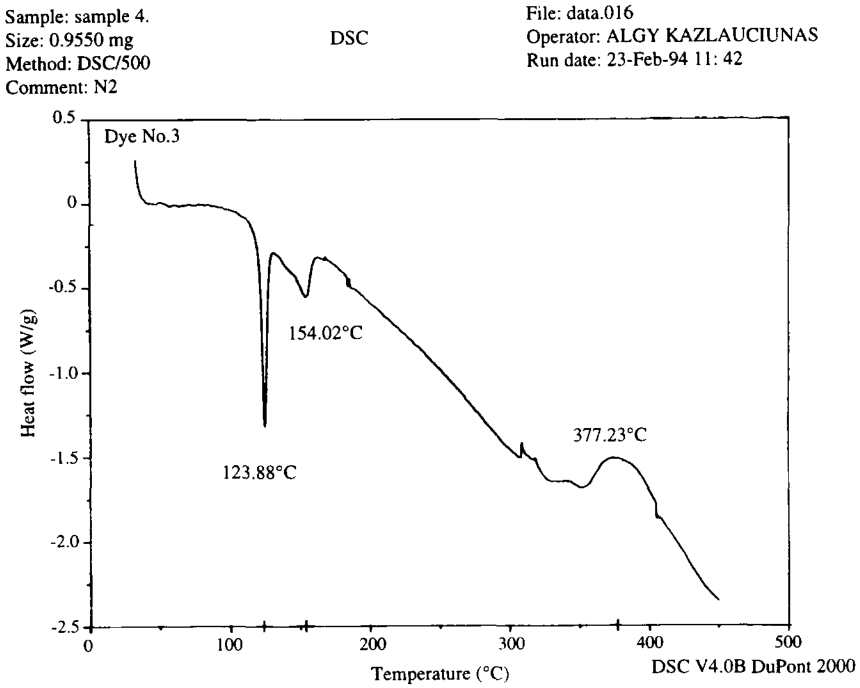


Fig. 3. DSC profile of the morphiline-oxide of the allyl chromophore (**I**).

Investigation of the molecular weights of the polymers

The intrinsic viscosity [η] was determined and the respective molecular weights calculated. The data presented in Table 1 show that the coloured polymers had lower molecular weights than the PAN obtained without dye. On the basis of these results it is possible to explain the lower percentage of chemically bonded dye **3** discussed in the previous section. Due to the lower molecular weight of the polymers obtained with dye **3**, most of the polymer was removed during the extraction chemically bonded to low-molecular weight fractions.

Investigations on the thermal stability of polymeric dyes

The thermal stability of the polymers was studied. From the data acquired it is possible to conclude that the participation of the dyes in the polymer chain did not affect the course of the thermal degradation of the polymers. The curves are identical with that of homopolymeric PAN obtained under the same conditions. It was observed that only the initial point of degradation shifted slightly to higher temperatures (Table 1).

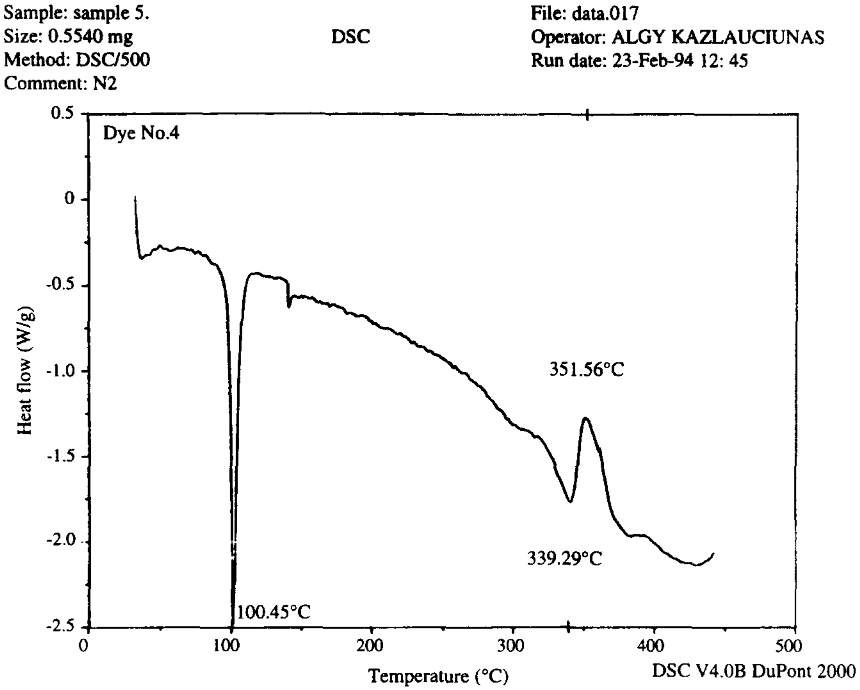


Fig. 4. DSC profile of the morphilino form of the allyl chromophore (I).

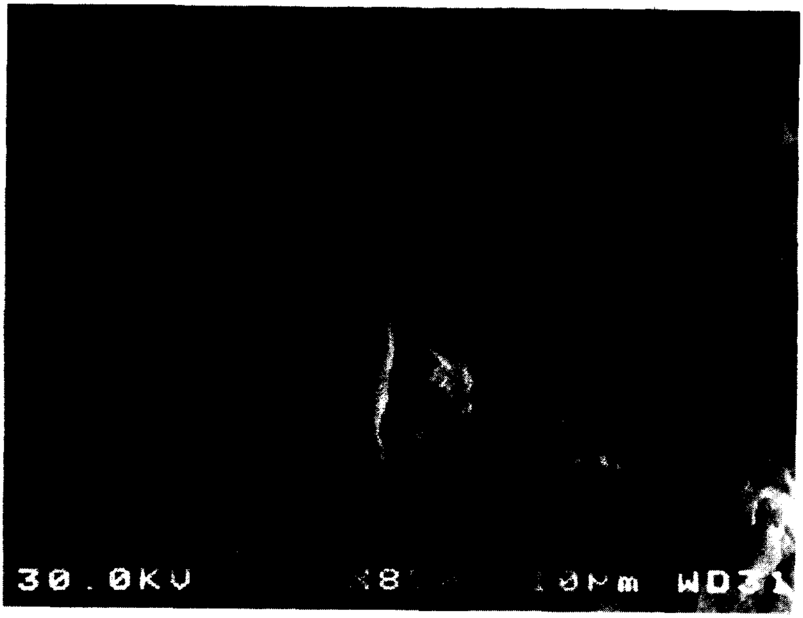


Fig. 5. Scanning electron micrograph of dye 1.

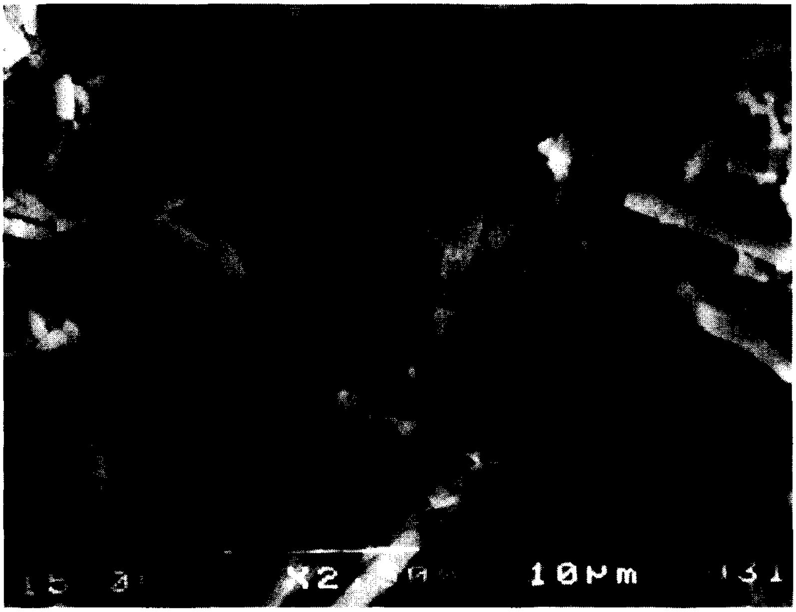


Fig. 6. Scanning electron micrograph of dye 2.

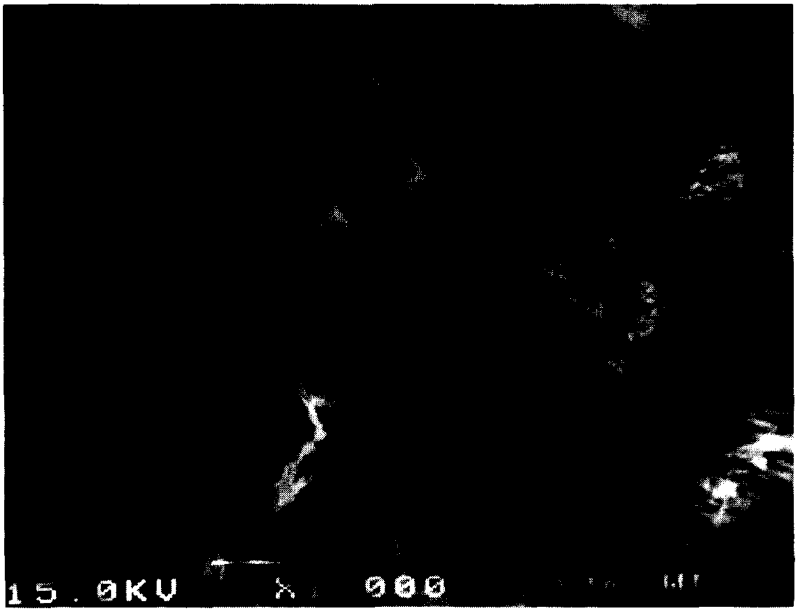


Fig. 7. Scanning electron micrograph of dye 3.

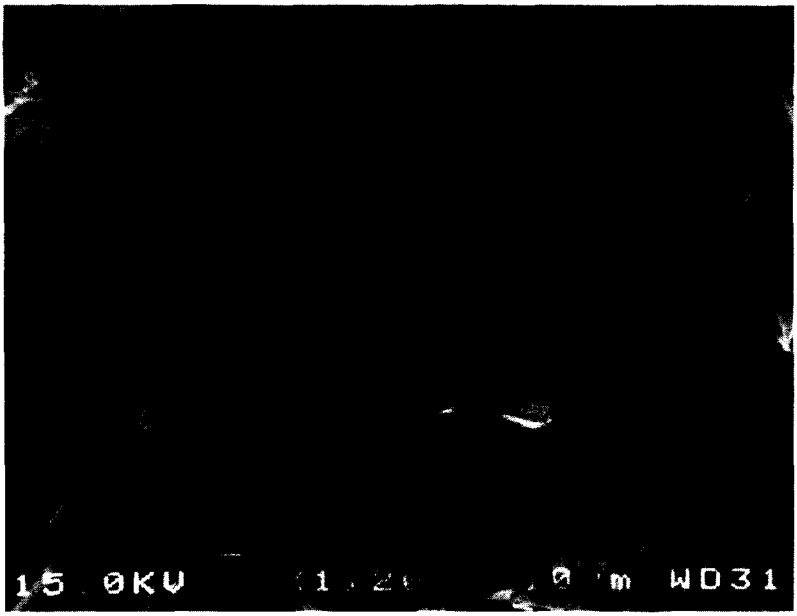


Fig. 8. Scanning electron micrograph of dye **4**.

CONCLUSIONS

Four *N*-allylaminoderivatives of naphthalimide co-polymerize with AN. The polymers thus obtained have resistence to solvents and fluoresce. More than 85–90% of the polymerizable dyes denoted **1**, **2** and **4** participated in co-polymerization and were bonded in the polymer chain. For dye **3**, 50% of the dye co-polymerized. Participation of the dyes in the polymerization led to copolymers with molecular weights in the order: pure PAN⇒**1**⇒**4**⇒**2**⇒**3**. The thermal stability of the dyes during the polymerization was satisfactory. Their presence in the co-polymer molecule did not affect the course of thermal decomposition of the coloured polymers.

On the basis of these results, it is possible to conclude that the investigated dyes are suitable for co-polymerization with AN.

ACKNOWLEDGEMENTS

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