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Małgorzata Okulska-Bozek^a; Tomasz Prot^a; Jerzy Borycki^a; Jerzy Kedzierski^b

^a Plastics and Rubber, Laboratory of Polymer Chemistry, Technical University of Radom, Institute of Tanning, Radom, Poland ^b Technical Military Academy of Warsaw, Institute of Technical Physics, Warsaw, Poland

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Preparation and evaluation of polyimide layers as materials for nematic liquid crystal orientation

by MAŁGORZATA OKULSKA-BOŻEK, TOMASZ PROT*,
JERZY BORYCKI and JERZY KĘDZIERSKI†

Technical University of Radom, Institute of Tanning, Plastics and Rubber,
Laboratory of Polymer Chemistry, Chrobrego 27, 26-600 Radom, Poland

†Technical Military Academy of Warsaw, Institute of Technical Physics,
00-908 Warsaw, Poland

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Ten polypyromellitimides, seventeen poly(imide esters) and six poly(imide amides) have been synthesized. The stability of 0.5% solutions of the poly(amic acids) in DMF, and the hardness, adhesion to glass and quality of nematic liquid crystal alignment of the polyimide layers using the *interference wedge* method have been tested. The relationship between the chemical structure of polyimides and their properties, especially the *alignment depth*, is discussed.

1. Introduction

The testing of liquid crystal alignment on solid surfaces is a very important problem in relation to both studies of the physico-chemistry of surfaces and obtaining desired electro-optical effects in the technology of liquid crystal displays (LCDs).

Although the surface alignment of nematic liquid crystals on polyimides is well established in the production of LCDs and many results in this field have been published during recent years, some questions are still open [1-4]. It is important to understand the effect of the chemical structure of the polyimides on the parameters important in LCDs such as orientation of the liquid crystals, thermal stability, dielectric constant and adhesion to ITO and glass.

Until now in the literature, mainly in patents, almost all basic groups of polymers have been suggested as special layers for liquid crystal orientation in LCDs. Spreading of a polymer solution on the surface, evaporation of the solvent, polymer crosslinking and finally rubbing of the surface is the most popular method to obtain such layers. In this way, various polymer materials have been used, for instance: polystyrene and its derivatives [5, 6], poly(vinyl alcohol) [5, 7, 8], polyarylates [9], esters and ethers of cellulose [10], polyesters [5, 8, 11], epoxide resins [12, 13], polyurethanes [14], polysilicones [8] and—most often—polyimides [1-4, 15-23].

Apart from this basic procedure, other methods are also available; among these are the following:

- the deposition of thin films of PTFE by cathode sputtering [24],
- the plasma polymerization of unsaturated fluorocarbons, such as C_2F_4 , C_4F_8 , C_6F_{12} etc [25, 26].

Beginning our work on obtaining well aligned layers for liquid crystal displays, our group decided to concentrate on the synthesis and evaluation of polyimides. Of all the groups of polymers, polyimides were expected to be the most promising, for many reasons [27-31]:

- the simplicity of thin layer preparation,
- high chemical and thermal resistance,
- very good adhesion to glass and oxide surfaces,
- wide possibilities of influencing alignment parameters by modification of chemical structure.

We assumed that the two-step polycondensation of suitable diamines and dianhydrides would be the principal method of polyimides synthesis [27-31]. We decided to synthesize and examine not only typical polyimides (polypyromellitimides), but also copolyimides:

- poly(imide esters): containing ester bonds besides imide rings in the polymer chain,
- poly(imide amides): polyimides containing amide bonds.

The main aim of our work was to find some correlation between the structure of the polymer and its physical properties important to LCD technology. We wished to compare the results for liquid crystal orientation using the *interference wedge* method with the results obtained by other methods.

* Author for correspondence.

Table 1. Basic materials, sources and purification methods.

	Basic material	Source	Purification method
1	acetic anhydride	Reachim	distillation with anhydrous sodium acetate
2	trimellitic anhydride	gift from the Institute of Industrial Chemistry in Warsaw	crystallization from acetic anhydride
3	pyromellitic anhydride	Koch-Light Lab	vacuum sublimation or crystallization from acetic anhydride
4	2,2-bis(4-hydroxyphenyl)propane [bisphenol A]	Merck-Schuchardt	—
5	2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane [bisphenol M]	gift from the Institute of industrial Chemistry in Warsaw	—
6	1,4-phenylenediamine	Reachim	vacuum distillation from zinc dust
7	1,3-phenylenediamine	BHD	vacuum distillation from zinc dust
8	2,4-diaminotoluene	Merck-Schuchardt	vacuum distillation from zinc dust
9	4,4'-diaminobiphenyl	Ferak	crystallization from aq. ethanol
10	4,4'-diaminodiphenylmethane	Fluka AG	crystallization from aq. ethanol
11	4,4'-(1,3-phenyldioxy)-diphenylamine	gift from the Jaroslaw Polytechnic Institute (Russia)	—
12	1,2-bis(4-aminophenyl)ethane	gift from the Jaroslaw Polytechnic Institute (Russia)	—
13	4,4'-diaminodiphenyl sulphone	Koch-Light Lab	crystallization from aq. ethanol
14	4,4'-oxybis(4-phenylthio)-diphenylamine	gift from the Jaroslaw Polytechnic Institute (Russia)	—
15	3,3'-dimethoxy-4,4'-diaminobiphenyl	Merck-Schuchardt	crystallization from aq. ethanol
16	4,4'-(2,2'-propyl-bis(p-phenyloxy))diphtalic anhydride	gift from the Jaroslaw Polytechnic Institute (Russia)	—
17	toluylene-2,4-diisocyanate (TDI)	Zachem-Bydgoszcz	vacuum distillation
18	4,4'-diisocyanatodiphenylmethane (MDI)	Merck-Schuchardt	—
19	1,6-hexamethylene diisocyanate (HMDI)	Merck-Schuchardt	vacuum distillation

2. Experimental

2.1. Basic materials, their sources and purification methods

The basic materials, their sources and the purification methods used are given in table 1.

2.2. Synthesis of polypyromellitimides

Polypyromellitimides were obtained by a two-step polycondensation. In the first step—the ring-opening polyaddition—10 per cent solutions of poly(amic acids) in dimethylformamide were prepared by reaction of

pyromellitic anhydride (2 per cent mol excess)† with the selected diamine. Poly(amic acids) were not isolated, but the specific viscosity of the prepared solutions was evaluated. Poly(amic acid) solutions (1 per cent in DMF) were spread on degreased glass substrates and then the solvent was evaporated. Polymer films prepared in this way were heated in a drier for one hour at a temperature

† From the literature [30] and our experience it was found that a 2 per cent mol excess enabled us to obtain the highest viscosity.

of about 80–100°C, one hour at a temperature of about 180–200°C and one hour at a temperature of 260°C. During this step the thermal imidization process (cyclo-dehydration process) took place. The course of these reactions is shown in Scheme 1.

The synthesis of poly(amic acids) from pyromellitic anhydride was effected according to methodology given in a prior paper [32]. Reactions between pyromellitic anhydride and the following amines were carried out: 1,4-phenylenediamine (PI-1), 1,3-phenylenediamine (PI-2), 4,4'-diaminodiphenylmethane (PI-3), 1,2-bis-(4-aminophenyl)ethane (PI-4), 4,4'-diaminodiphenyl sulphone (PI-5), 4,4'-diaminobiphenyl (PI-6), 3,3'-dimethoxy-4,4'-diaminobiphenyl (PI-7), 4,4'-oxybis-(4-phenylthio)diphenylamine (PI-8), 4,4'-(1,3-phenyldioxy)diphenylamine (PI-9), 2,4-diaminotoluene (PI-10).

2.3. Preparation of poly(imide esters)

To obtain the poly(imide esters) it was necessary to synthesize dianhydrides containing ester bonds in the molecules. Two methods of preparation were used. Reaction of bisphenol diacetate and trimellitic anhydride was the first. Diacetates were obtained by the reaction of acetic anhydride with bisphenols (hydroquinone, resorcin, bisphenol A, bisphenol M) in the presence of sulphuric acid [32]. They were then heated with trimellitic anhydride at 260–280°C to give bisester anhydrides (Scheme 2, (1) and (2)).

The dianhydride from hydroquinone and trimellitic anhydride was the only one obtained in this way. In the case of the other three reactants (resorcin, bisphenol A, bisphenol M), the second step of synthesis failed.

The second method used was the reaction between trimellitic anhydride chloride and selected bisphenols (bisphenol F, bisphenol A, bisphenol M, 4,4'-

dihydroxybiphenyl), proceeding in accordance with Scheme 3 [32, 33].

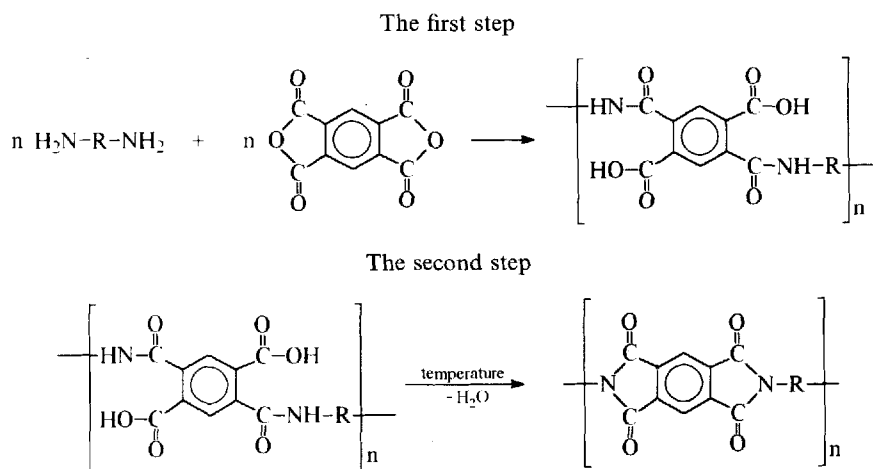
The methodology of these syntheses was described in detail in a prior article [32]. The following compounds were obtained by the second method (Scheme 4).

These bisester anhydrides (I)–(IV) and selected diamines were used as substrates for preparation of poly(amic esters). Poly(amic esters) were synthesized by a two-step reaction proceeding in an analogous way to that in the synthesis of the polypyromellitimides. The following scheme shows the course of this process (Scheme 5) [28, 29, 31].

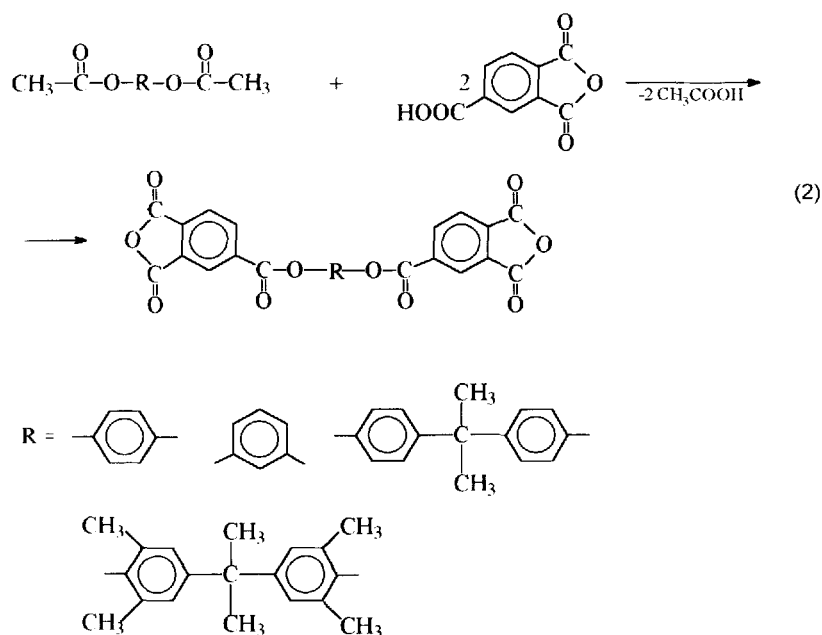
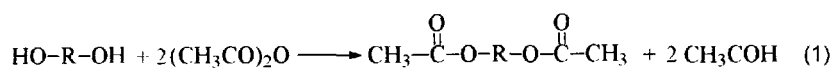
The following series of syntheses were conducted between (I) and 1,2-bis(4-aminophenyl)ethane (PEI-1), 1,4-phenylenediamine (PEI-2), 1,3-phenylenediamine (PEI-3), 4,4'-diaminobiphenyl (PEI-9), 3,3'-dimethoxy

Table 2. Some details about the bisester anhydrides.

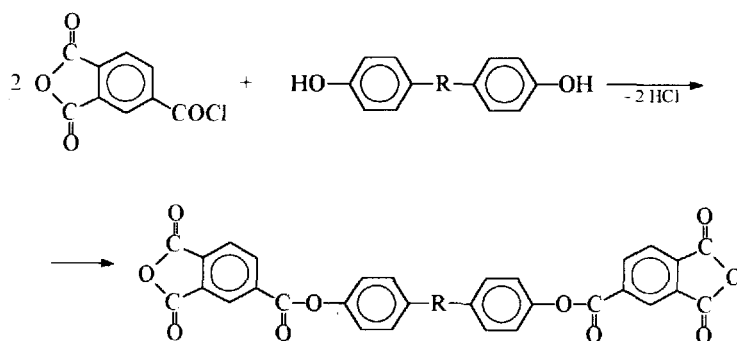
Symbol for bisester anhydride	Purification process	Yield/%	$T_m/^\circ\text{C}$
I	crystallization from dioxan	63.3	275–277
II	crystallization from acetic anhydride	72.9	198–201
III	precipitation with n-hexane from acetic anhydride–benzene solution	85.0	190–192
IV	precipitation with n-hexane from acetic anhydride–benzene solution	74.6	205–210



Scheme 1. Two-step polycondensation of dianhydride and diamine.



Scheme 2. Preparation of bisester anhydrides (method 1) by the reaction of bisphenol diacetates with trimellitic anhydride.



Scheme 3. Preparation of bisester anhydrides (method 2)—reaction of bisphenol and trimellitic anhydride chloride.

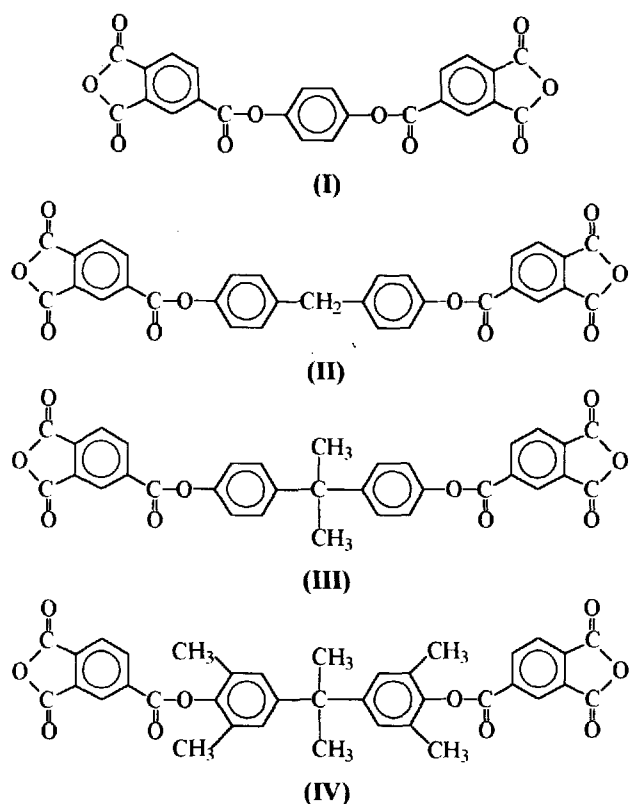
-4,4'-diaminobiphenyl (PEI-10), 4,4'-(1,3-phenyldioxy)-diphenylamine (PEI-15), between (III) and 2,4-diaminotoluene (PEI-4), 1,2-bis(4-aminophenyl)ethane (PEI-5), 1,4-phenylenediamine (PEI-6), 1,3-phenylenediamine (PEI-7), 4,4'-oxybis(4-phenylthio)diphenylamine (PEI-8), 4,4'-diaminobiphenyl (PEI-11), 3,3'-dimethoxy-4,4'-diaminobiphenyl (PEI-12), between (IV) and 4,4'-diaminobiphenyl (PEI-13), 4,4'-diaminodiphenylmethane (PEI-14), and between (II) and 4,4'-diaminobiphenyl (PEI-16), 2,4-diaminotoluene (PEI-17).

2.4. Preparation of poly(imide amides)

The third group, poly(imide amides), was obtained in two different ways. The first was the two-step condensation of trimellitic anhydride chloride and diamines (Scheme 6) [34–37].

These reactions proceeded according to the methodology described in [32]. The second method was a one-step reaction between trimellitic anhydride and diisocyanate with carbon dioxide evolution (Scheme 7) [38–41].

The detailed methodology was described earlier [41].



Scheme 4. Structural formulae of bisester anhydrides.

The poly(imide amides) obtained were made from trimellitic anhydride chloride and 4,4'-diaminodiphenylmethane (PAI-1), 4,4'-diaminobiphenyl (PAI-2) and 2,4-diaminotoluene (PAI-3), and from

trimellitic anhydride and toluylene-2,4-diisocyanate (PAI-4), 4,4'-diisocyanatediphenylmethane (PAI-5) and 1,6-hexamethylene diisocyanate (PAI-6).

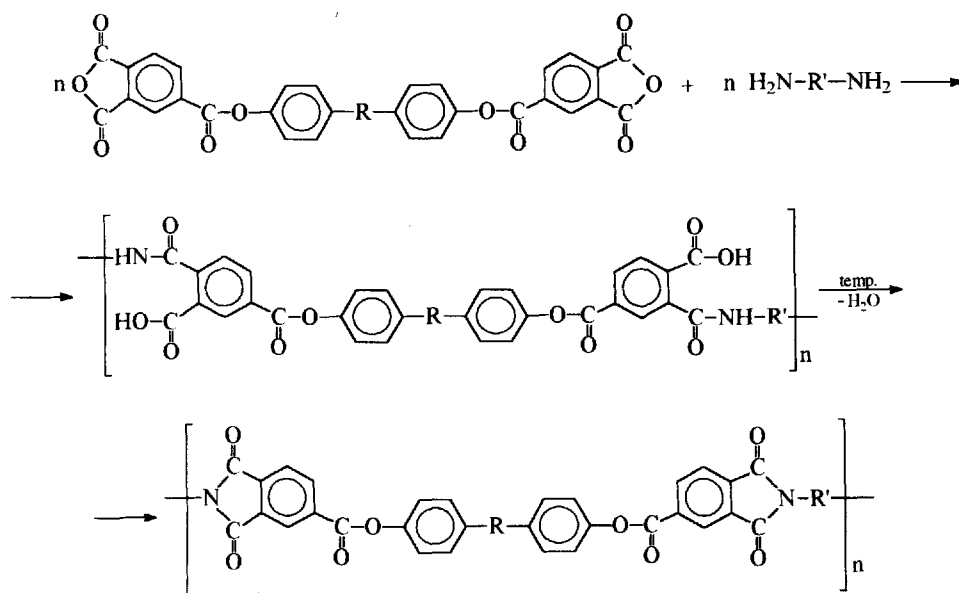
2.5. Measurements

The stability of 0.5 per cent polyamic acid solutions in DMF was tested by viscometry using an Ubbelohde viscometer, at 25°C. Relative hardness was evaluated by König pendulum according to Polish Standards. The ratio of oscillation decay time of the pendulum resting at the tested layer to oscillation decay time of the pendulum resting at the glass plate is determined in this method. The polymer layers should be prepared using sodium glass plates of dimensions 100 × 100 × 2–3 mm, washed and dried in a suitable way. The value of the relative hardness (X) is calculated from the formula:

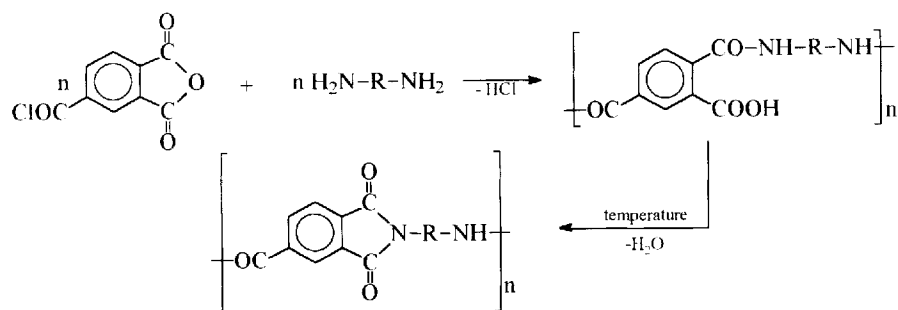
$$X = \frac{a}{b}$$

where X = relative hardness by König pendulum, a = oscillation decay time of König pendulum at the tested layer (s), and b = glass constant (250 ± 10 s). The higher the value of the oscillation decay time at the tested layer, the harder is the layer.

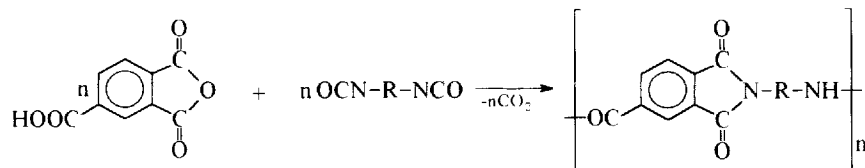
Adhesion to glass was also examined according to Polish Standards. To evaluate adhesion to glass, a special roller knife built from six parallel cutting edges arranged at 1 mm spacing was used. First, the tested polyimide film was cut at a distance of about 20 mm from the plate edge. Then the second incision, perpendicular to the first set, was made. A net with 25 squares was created. The degree of destruction of the polymer layer was observed



Scheme 5. Preparation of poly(ester imides) by two-step polycondensation.



Scheme 6. Two-step synthesis of poly(imide amides) from trimellitic anhydride chloride and diamines (method 1).



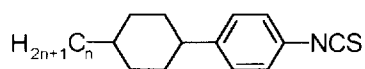
Scheme 7. One-step synthesis of poly(imide amides) from trimellitic anhydride and diisocyanate (method 2).

visually using a magnifying lens $\times 5$. Adhesion degree was described on the scale 1 \rightarrow 4. The higher the value of the adhesion degree the worse the adhesion is.

To evaluate the usefulness of various polyimides for planar alignment of samples of nematic liquid crystals (NLC), a new method (*interference wedge method*) was proposed by us. The idea was based on estimation of the *alignment depth* in the liquid crystal caused by a given polyimide. To do this, a liquid crystal wedge was used [42, 43].

Thin polyimide layers (about 1 μm) on plane-parallel glass plates were prepared by spreading 0.5 per cent poly(amic acid) solutions in DMF by use of a centrifuge at 2000 r.p.m. during 2 min. Heating for one hour at 80°C to evaporate the solvent and for two hours at 200°C to cure the polymer was the next step. After this, the polyimide films on the glass plates were subjected to a unidirectional rubbing operation. Soft rubbing by a rotating roller covered with batiste fabric was used [44]. Thanks to the presence of the unidirectional microscratches on the surface of cured polyimide it is possible to obtain an identical director alignment, parallel to scratches, in the sample of nematic liquid crystal.

To construct a liquid crystal wedge cell, glass plates of dimensions 2 cm \times 4 cm and a cylindrical spacer of diameter d from 0.3 to 1.2 mm were used (figure 1). In our examination, the liquid crystal 6CHBT was used [45]:



($n = 6$) 12.5 N 43.05 I

In such a liquid crystal cell, the optic axis is parallel to the wedge edge (figure 1). The cell was put on the polarizing microscope stage (x,y). In this way, the birefringent wedge was examined microscopically [46].

In the field of view of the microscope, in a monochromatic parallel light beam, the interference fringes of equal thickness and parallel to the edge of the liquid crystal wedge can be observed. The interference fringes were observed either in the ocular of the microscope or on the screen of the monitor of a TV camera. These fringes or striae are regarded as a result of interference of the ordinary and extraordinary rays going through the birefringent layer with gradually changing thickness.

The observed striae are localized on the top surface of the liquid crystal cell. The block diagram of the measurement scheme for testing a polyimide's ability to orient the liquid crystal is presented in figure 2.

Dependent upon the type of polyimide, various extents of well-formed interference striae appeared at a certain distance x_j from the edge of the wedge. The aligned layer of nematic liquid crystal of thickness d_j was responsible for the j -stria (figure 3). The thickness d_j was named the *alignment depth* of liquid crystal created by the polyimide film. This parameter d_j can be defined and interpreted in the following way:

1. using a liquid crystal wedge cell of aligned thickness d_j we obtain a sample of nematic liquid crystal with the properties of a uniaxial crystal with a well-defined optic axis (4 extinction positions for a 360° rotation of the microscope stage);
2. it can be assumed that d_j is a measure of surface anchoring strength;

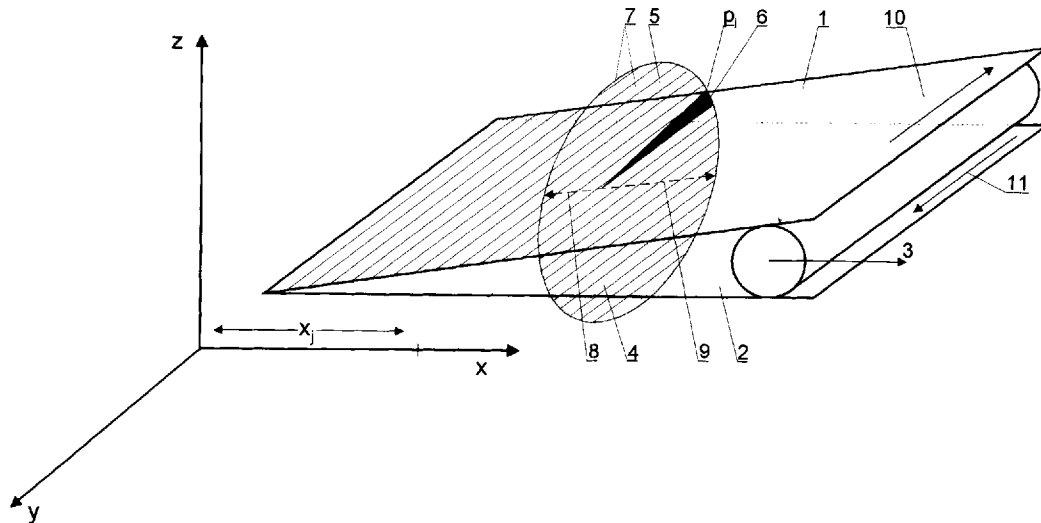


Figure 1. The field of view in the ocular of the measurement scheme: 1,2 – glass plates covered with rubbed polyimide layer, 3 – spacer, 4 – aligned liquid crystal, 5 – the picture apparent in the ocular, 6 – reference indicator (point p_i), 7 – interference striae, 8,9 – displacement direction of interference striae in the wedge moving in the direction of the x axis, 10,11 – directions of anti-parallel rubbing.

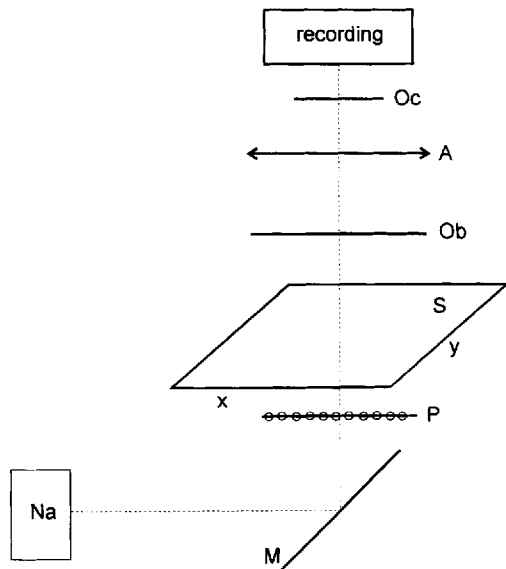


Figure 2. The system for measurement of alignment depth in a NLC by a polyimide film: Oc, ocular; A, analyser; Ob, objective; S, sample on the microscope stage (x,y); P, polarizer; M, mirror introducing monochromatic light to the field of view of the polarizing microscope; Na, sodium lamp; recording—eye of the experimenter, TV camera or photo-camera.

3. the alignment depth d_j is directly proportional to the anchoring energy.

To estimate the value of d_j , the following parameters were defined:

(a) the number of very good, clear striae, appearing

with very good alignment of the liquid crystal, is characterized by an alignment depth d_1 ; this means that the last very good stria appears at the distance x_1 from the edge of the liquid crystal wedge at a thickness of LC equal to d_1 (figure 4);

(b) the number of reasonably clear striae, relating to adequate LC alignment, is characterized by the alignment depth d_2 ; this means that the last clear stria appears at the distance x_2 from the edge of the LC wedge at a thickness of LC equal to d_2 (figure 5).

The values of alignment depths d_1 and d_2 were calculated from the following formulae:

$$d_1 = \frac{d(x_1 - x_0)}{x_s - x_0}$$

$$d_2 = \frac{d(x_2 - x_0)}{x_s - x_0}$$

where d = cylindrical spacer diameter, d_1, d_2 = alignment depths of NLC developed by polyimide, x_s = spacer position, x_0 = position of the edge of liquid crystal cell, x_1 = position of last interference stria corresponding to the best liquid crystal alignment, x_2 = position of last interference stria corresponding to reasonable liquid crystal alignment. All measurements were conducted at room temperature (25°C).

3. Results and discussion

The testing of selected physico-chemical properties of prepared polyimides and polyimide layers.

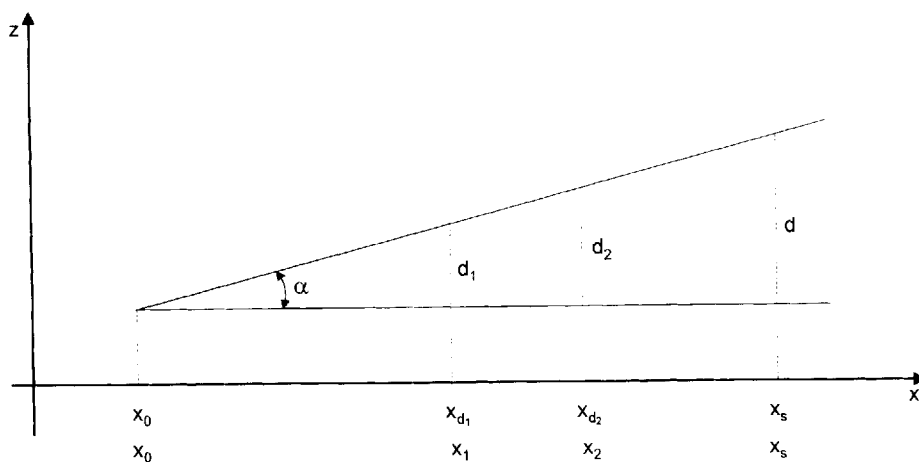
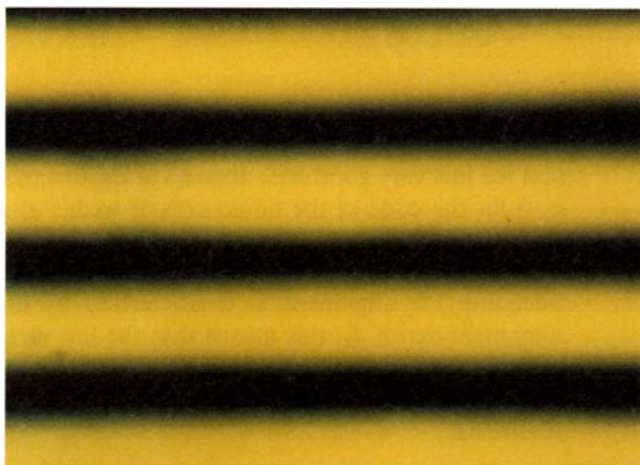
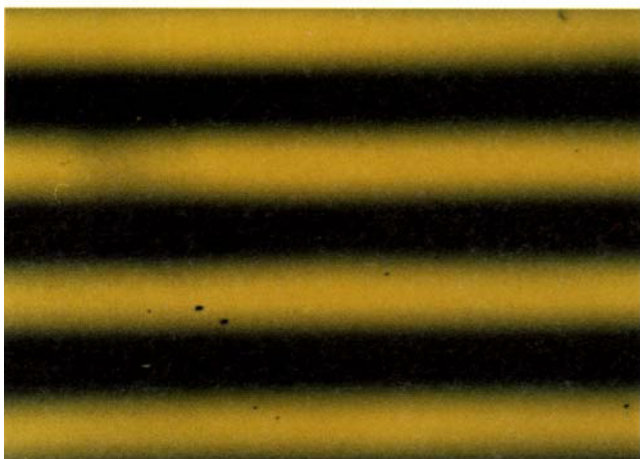


Figure 3. The geometry of the liquid crystal wedge, $\tan\alpha = d_1/(x_1 - x_0) = d_2/(x_2 - x_0) = d/(x_s - x_0)$.

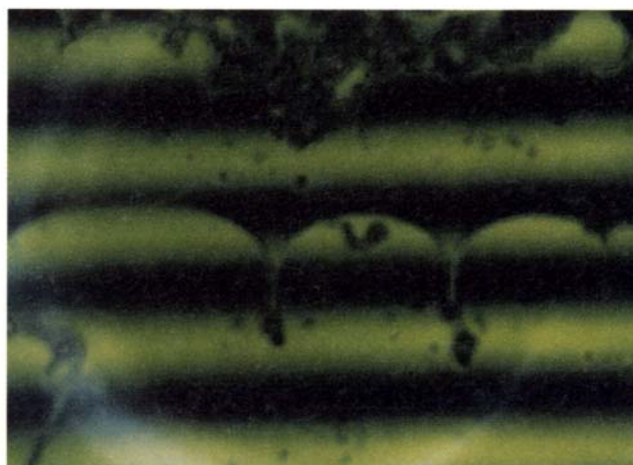


(a)

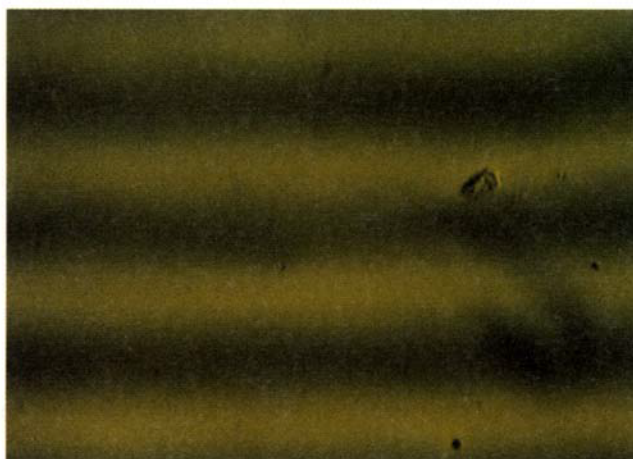


(b)

Figure 4. Very good, clear interference striae corresponding to very good alignment of the liquid crystal.



(a)



(b)

Figure 5. Reasonably clear interference striae corresponding to adequate alignment of the liquid crystal.

3.1. Stability of poly(amic acid) solutions

Results of viscometry measurements are listed in table 3.

The solution behaviour of poly(amic acids) is still probably the least understood aspect of the soluble polyimide precursor. Upon combination of the monomers an increase in the viscosity up to the equivalence point is observed, followed by a decrease in the solution viscosity as a function of time. Although the initial increase in solution viscosity is quite expected, the

Table 3. Specific viscosity of 0.5 per cent poly(amic acid) solutions.

Sample symbol	Specific viscosity (η) after t (h)				
	0.5	1	1.5	2	5
PI-1	0.410	0.513	0.221	0.184	0.182
PI-2	0.381	0.395	0.396	0.396	0.387
PI-3	0.510	0.572	0.549	0.548	0.537
PI-4	0.147	0.161	0.178	0.178	0.158
PI-5	0.024	0.066	0.101	0.115	0.112
PI-6	0.341	0.346	0.351	0.351	0.349
PI-7	0.175	0.179	0.181	0.180	0.181
PI-8	0.112	0.088	0.088	0.086	0.087
PI-9	0.105	0.109	0.112	0.101	0.110
PI-10	0.461	0.712	0.530	0.528	0.528
PEI-1	0.117	0.130	0.141	0.164	0.172
PEI-2	0.920	1.120	1.090	0.96	0.91
PEI-3	0.290	0.310	0.325	0.321	0.322
PEI-4	0.078	0.110	0.113	0.110	0.112
PEI-5	0.124	0.156	0.106	0.089	0.054
PEI-6	0.511	0.416	0.411	0.412	0.402
PEI-7	0.330	0.293	0.291	0.290	0.287
PEI-8	0.288	0.272	0.276	0.281	0.276
PEI-9	0.256	0.263	0.281	0.281	0.279
PEI-10	0.153	0.158	0.158	0.158	0.156
PEI-11	0.454	0.537	0.527	0.525	0.512
PEI-12	0.246	0.259	0.259	0.258	0.254
PEI-13	0.102	0.115	0.117	0.119	0.111
PEI-14	0.073	0.076	0.088	0.086	0.085
PEI-15	0.144	0.147	0.156	0.155	0.153
PEI-16	0.439	0.463	0.437	0.436	0.429
PEI-17	0.136	0.166	0.169	0.167	0.159
PAI-1	0.060	0.070	0.078	0.080	0.080
PAI-2	0.045	0.054	0.068	0.071	0.070
PAI-3	0.060	0.068	0.078	0.079	0.078

subsequent decrease in solution viscosity has been generally interpreted in terms of hydrolytic molecular weight degradation. Careful examination of such systems led to the discovery that the initially high viscosities reflected average molecular weights much higher than predicted by the monomer stoichiometry. The molecular weights then decreased as a function of time and temperature to a molecular weight in accordance with the molecular weight calculated by Carother's equation [47]. Re-equilibration can be attributed to the existence of a polymer-monomer equilibrium [30].

The results from table 3 show that poly(amic acids) prepared from pyromellitic anhydride had a lower stability in comparison with poly(amic acids) obtained from anhydrides containing ester or amide groups. The second step of the polyimide synthesis, cyclodehydration or imidization, is achieved by heating the poly(amic acids) above 250°C. It is expected that good layers can be created by polymers with a viscosity parameter above 0.3. However, many values of viscosity were lower than this, and we obtained good films with thicknesses about 5–10 μm . Polyimide layers with equal thickness were used for further testing.

3.2. König test of hardness

The selected results of hardness measurements are presented in table 4. The films of 5–10 μm were used for these measurements. Therefore, all the tested polyimide surfaces are characterized by very high hardness values (0.80–0.95), and it seems that this property is rather independent of polyimide structure.

3.3. Adhesion to glass

During adhesion tests by the cut method, it was found that all the synthesized polyimides were characterized by good and very good adhesion to glass (the value of adhesion degree was equal to 1). No significant effect of the chemical structure of the polyimides on adhesion to glass was noticed.

3.4. Ability to align liquid crystals

The results of the *alignment depth* measurements are collected in table 5. The value d_m is the arithmetic mean of d_1 and d_2 .

Table 4. Results of measurements of hardness of polyimide layers.

Polypyromellitimides		Poly(ester imides)		Poly(amide imides)	
sample symbol	hardness	sample symbol	hardness	sample symbol	hardness
PI-2	0.87	PEI-2	0.93	PAI-1	0.89
PI-3	0.83	PEI-3	0.87	PAI-2	0.80
		PEI-5	0.90	PAI-3	0.87
		PEI-6	0.87	PAI-4	0.93
		PEI-7	0.87	PAI-5	0.93
		PEI-8	0.92		

Table 5. Alignment depth data for the polyimide layers prepared.

Sample symbol	d_1 /mm	d_2 /mm	d_m /mm
Polypyromellitimides			
PI-1	0.42	0.49	0.45
PI-2	0.33	0.52	0.45
PI-3	0.34	0.37	0.36
PI-4	0.45	0.49	0.47
PI-5	0.37	0.42	0.39
PI-6	0.19	0.27	0.23
PI-7	0.28	0.33	0.31
PI-8	0.36	0.51	0.44
PI-9	0.11	0.23	0.17
PI-10	0.79	0.91	0.84
Poly(ester imides)			
PEI-1	0.41	0.51	0.46
PEI-2	0.34	0.43	0.38
PEI-3	0.22	0.50	0.36
PEI-4	0.24	0.44	0.34
PEI-5	0.37	0.45	0.41
PEI-6	0.24	0.48	0.36
PEI-7	0.48	0.50	0.49
PEI-8	0.54	0.59	0.56
PEI-9	0.15	0.39	0.27
PEI-10	0.13	0.17	0.15
PEI-11	0.04	0.07	0.06
PEI-12	0.03	0.05	0.04
PEI-13	0.04	0.08	0.06
PEI-14	0.19	0.34	0.26
PEI-15	0.12	0.22	0.17
PEI-16	0.36	0.42	0.39
PEI-17	0.32	0.44	0.38
Poly(amide imides)			
PAI-1	0.56	0.62	0.59
PAI-2	0.42	0.61	0.51
PAI-3	0.19	0.43	0.31
PAI-4	0.35	0.51	0.43
PAI-5	0.28	0.46	0.37

As can be seen in table 5, all of the synthesized polyimides were able to align liquid crystal layers. However, the *alignment depth* varied from 0.04 to 0.8 mm. It was concluded that polyimides PI-8, PI-10, PEI-14, PEI-16 and PEI-17 had very high alignment parameters. Polyimides PI-7, PI-9, PEI-9 and PAI-1 have a rather lower ability to give alignment. Analysis of the chemical structure of the polyimides and of their alignment ability supports the thesis [46, 47] that polyimides containing short groups such as: $-\text{CH}_2-$, $-\text{O}-$, $-\text{S}-$ or $-\text{SO}_2-$ between stiff aromatic segments have the best alignment parameters.

4. Conclusions

1. Solutions of polyamic acids prepared from pyromellitic anhydride have a lower stability than polyesteramic and polyamidoamic acids; the process of

hydrolytic molecular weight degradation occurs faster. Solutions of polyamidoamic acids and poly-(amide imides) possess the best stability.

2. The higher the molecular weight of a polyamic acid, the faster in the process of decrease in solution viscosity.
3. All of the synthesized polyimides, sometimes in spite of a low specific viscosity, possess the ability to form good films.
4. Polyimide films on glass plates have a high relative hardness as tested by König pendulum ($x = 0.80-0.95$).
5. All polyimide films were characterized by good and very good adhesion to glass (the value of adhesion degree was equal to 1).
6. All of the synthesized polyimides have the ability to align a liquid crystal; the measured *alignment depth* has values from 0.04 to 0.8 mm. Polyimides, containing short groups such as $-\text{CH}_2-$, $-\text{O}-$, $-\text{S}-$ or $-\text{SO}_2-$ between stiff aromatic segments in the polymer chain, possess the best alignment parameters; the *alignment depth* for these polyimides is about 0.3–0.4 mm.

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