

Determination of the thickness and optical constants of polyarylates with heterocyclic side chain group

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Investigation of the optical properties of the novel polyarylates with heterocyclic side chain groups is reported. Optical properties of the polymers obtained have been measured. Mechanical and thermal properties are also presented. Refractive index $n(\lambda)$ and susceptibility $\chi^{(1)}$ have been determined for different compositions of polymers.

1. Introduction

A continuous growth of polymer applications in telecommunication as materials for fiber optics [1]–[4] and photonic devices is recently observed. Polymers with second order optical nonlinearity play here an important role. Active waveguides constructed from polymers are used for photonic modulation of optical signals [5]–[7]. It is easy to obtain thin films of polymer almost on each substrate with a spin-coating method or conventional microlithography. These techniques enable construction of polymer photonic devices much cheaper than by traditional methods. Other interesting properties of polymers are low dielectric dispersion and high nonlinearity, which allow high speed of switching between optics fibers.

Work on synthesising polymers with high optical nonlinearity has been continued for several years. Guest-host, side-chain, main-chain and cross-linked polymers with different chromophores [8], [9] are fabricated by thermal and photochemical methods. Synthesis of amorphous polymers with a variety of side group, substituting typical electron accepting groups has been successfully performed [10].

Current research is concentrated on synthesis of polymers with potential second order optical nonlinearity based on several polyarylate and bisbenzylidoneketones.

The synthesis of polyarylate studied in this paper is based on special monomer Schiff's bases obtained from the condensation reaction between 2,4-dihydroxybenzaldehyde, formylbisphenol and 4 or 5 substituted 2-aminothiazoles. They have potential second-order nonlinear optical properties.

In this work, the results of measurements of the refractive indices $n(\lambda)$ and electric susceptibilities for new composites of polymers with high optical nonlinearity are presented. Preliminary results concerning this series of polymers were presented earlier [11].

2. Characteristic of polymers

Polymers investigated in this paper may be divided into two main groups: PAR-1 and PAR-2, according to their chemical structure (Fig. 1). The polymers with signatures Par 1- n , 2- n are composed of the first group (PAR-1) and different dyes – monomers M (1 and 2 correspond to a dye "a" and "b", respectively, see Tab. 1). The polymers with signatures Par 5- n , 6- n , 7- n are composed of the second group (PAR-2) where 5, 6 and 7 correspond to dye "a" and "b" and "d", respectively. Chemical structure and meaning of parameters m and n are shown in Fig. 1 and Tab. 1.

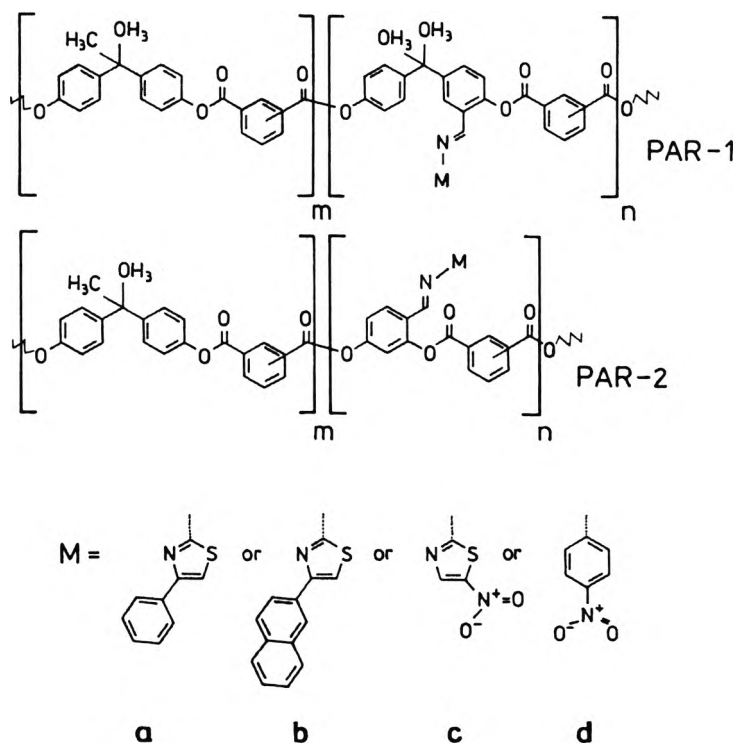


Fig. 1. Structure of polymers with dyes M ($m = 1, 2, 3$, $n = 1, 2, 3$). **a** – 4-phenylthiazol-2-yl-, **b** – 4-naphthylthiazol-2-yl-, **c** – 5-nitrothiazol-2-yl-, **d** – 4-nitrophenyl-.

Table 1. Polymers with dyes.

Main group of a polymer	Dyes (monomers M)	Calculating notation	<i>m</i> [%]	<i>n</i> [%]
PAR-1	a	Par 1- <i>n</i>	99, 98, 96, 90	1, 2, 4, 10
	b	Par 2- <i>n</i>	98	2
	c, d	—	—	—
PAR-2	a	Par 5- <i>n</i>	99	1
	b	Par 6- <i>n</i>	99, 98	1, 2
	c	—	—	—
	d	Par 7- <i>n</i>	99	1

For interfacial polymerisation reactions we have used several special amine monomers, derivatives of substituted aminothiazoles of the general formula presented in Fig. 1. Synthesis of the monomers was carried out using the condensation reaction between the carbonyl compound (2,4 dihydroxybenzaldehide or formybisphenol and the amine in a refluxing solvent). Polyarylates can be obtained in interfacial polycondensation reaction from the special monomers and bisphenol A.

All mechanical properties of these polymers were described earlier [12]. However, for the sake of convenience, we have induced them again in brief in Tab. 2. One can find more information elsewhere [12]. In each case the values obtained were compared with the results from Par 0 (grey row) — polyarylate synthesised on bisphenol A base.

Table 2. Mechanical and thermal properties of polymer films.

Film symbol	Tensile strength [MPa]	Intrinsic viscosity η [100 cm ³ /g ²]	Glass temperature [°C]	Temperature of decomposition [°C]	Fastest decomposition temperature [°C]
Par 1-1	28.17	1.65		340	520
Par 1-2	44.75	0.74	117.5	340	460
Par 1-4	34.06	1.02		320	460
Par 1-10	26.55	0.81	123.0	310	440
Par 2-2	24.20	1.14		350	480
Par 5-1	35.79	1.42		340	460
Par 6-1	59.07	1.37		350	460
Par 6-2	33.92	1.14	122.0	340	480
Par 7-1	33.81	1.98		330	480
Par 0	42.19	1.11		340	460

3. Determination of refractive index for thin polymer films

Thin polymer films were prepared by pouring the solutions on Si glasses. A scheme of the film is given in Fig. 2. The transmission of light for these pre-prepared samples was measured by UV/VIS Perkin Elmer lambda 40 spectrometer in the range

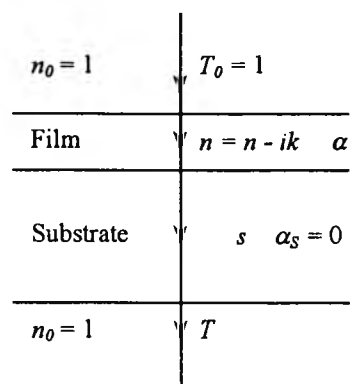


Fig. 2. Scheme of sample.

from 350 nm to 1100 nm. For shorter wavelengths, the absorption of the sample was too big. To determine refractive index $n(\lambda)$ and thickness of polymer film the interference effects of transmitted and reflected waves (arising at different environmental borders of glass, polymer and air) have to occur. To reach large difference between refractive indices of substrate and film, polymers were poured on Si glass. If thickness and density are uniform, it is possible to observe interference fringes in transmission spectra (Fig. 3). If the thickness of a film was not uniform there would

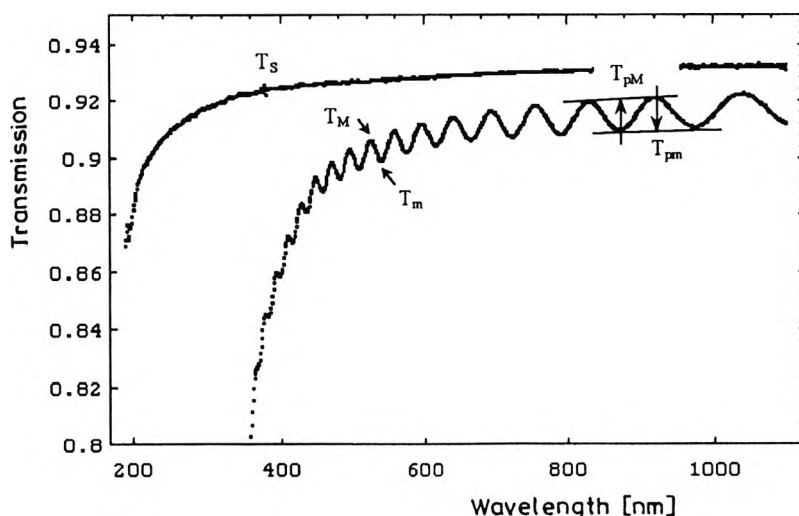


Fig. 3. Transmission of Si glass substrate T_s . Transmission of the sample with poured polymer layer, T_M and T_m , T_{pM} and T_{pm} at linear approximation.

not be any interference effects and transmission curve would be smooth. Interference fringes are used to determine optical constants of a film. The basic equation describing creation of fringes can be written as

$$2nd = m\lambda \quad (1)$$

where m is an integer number for maximum and half-integer for minimum of transmission. Equation (1) contains information about refractive index n and film thickness d . Considering the thick substrate alone in the absence of a polymer film, the interference free transmission is given by the well known formula

$$T_s = \frac{(1-R)^2}{1-R^2} \tag{2}$$

where R is the reflection coefficient.

The refractive index s of a substrate can be determined by measuring clear glass transmission T_s . Substrate transmission T_s corresponding to the substrate refractive index s at normal incidence is given by the relation

$$T_s = \frac{2s}{s^2 + 1}$$

Hence it appears that

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2} \tag{3}$$

Table 3. An example calculated for polymer Par 1-10 (s independent of λ). The average value of the thickness calculated from d_2 is used to obtain the final refractive index n_2 as a function of wavelength λ .

s	λ [nm]	T_M	T_m	n_1	d_1 [nm]	m	d_2 [nm]	n_2
1.4868	1060.1	0.927	0.899	1.594		7	2328	1.566
	989.09	0.925	0.8977	1.591		7.5	2331	1.566
T_s	929.01	0.924	0.897	1.59	2408	8	2338	1.568
0.9262	871.09	0.922	0.8961	1.587	2352	8.5	2333	1.563
	826.12	0.921	0.895	1.586	2398	9	2344	1.569
	783.75	0.919	0.8941	1.583	2516	9.5	2351	1.571
	745.5	0.917	0.893	1.583	2461	10	2355	1.573
	709.91	0.915	0.8915	1.58	2432	10.5	2359	1.573
	679.95	0.913	0.89	1.58	2488	11	2367	1.578
	650.05	0.911	0.8882	1.578	2469	11.5	2368	1.578
	624.08	0.909	0.886	1.579	2419	12	2371	1.58
	598.22	0.907	0.8843	1.577	2398	12.5	2370	1.578
	578.15	0.905	0.882	1.58	2481	13	2379	1.586
	557.08	0.902	0.8792	1.578	2550	13.5	2383	1.587
	539.06	0.899	0.876	1.579	2533	14	2390	1.593
	520.8	0.896	0.8735	1.579	2523	14.5	2392	1.594
	505.63	0.893	0.871	1.58	2557	15	2400	1.601
	489.86	0.889	0.8677	1.577	2650	15.5	2407	1.602
	476.35	0.886	0.862	1.586				
	461.28	0.858	0.8564	1.494				
Average d					2477		2369	
Standard deviation					76.22		21.82	

To calculate refractive index profile of polymer $n(\lambda)$, it is necessary to determine the maximum T_M and minimum T_m values of transmission curve for each wavelength (Tab. 3).

Because of the fact that for actual wavelength there exists either maximum or minimum only, one has to calculate the other side value of transmission (T_{mM} or T_{pm}) using linear approximation method (Fig. 3 and numbers in shaded area of Tab. 3)

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (4)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (5)$$

and the transmission values T_M or T_m are in fact T_{pM} or T_{pm} .

Values of refractive index n_1 calculated from Eq. (4) are shown in Tab. 3. In order to simplify this example, all calculations the results of which are collected in Tab. 2 were carried out for s constant, independent of λ and for polymer Par 1-10.

However, actually to reach higher accuracy, no approximation of the substrate transmission T_s by its maximum value (as was the case in [9] and in Tab. 3) was made. Instead, we have used the values measured by a spectrophotometer. Hence, now the refractive index of substrate s is no longer constant but depends on the wavelength of light λ . Values n_1 (Tab. 3) were calculated from experimental data at points T_M and T_m . The precisely defined thickness d of a thin polymer film is necessary to improve accuracy in determination of $n(\lambda)$.

If n_1 and n_2 are the refractive indices at two adjacent maxima (or minima) for λ_1 and λ_2 , it is easy to determine from Eq. (1) the film thickness d_1 for the entire range of wavelengths from 460 nm to 1060 nm

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (6)$$

Values of thickness d_1 of polymer film (Tab. 3) determined from Eq. (6) show significant dispersion (changing with wavelength). The fact of the accuracy of determining the thickness of polymer film d_1 being not too high is due to the significant error in refractive index $n_1(\lambda)$. That is why the average value d was calculated from values d . This average value d and $n_1(\lambda)$ are used to define interference row m (order numbers of extremes) from Eq. (1). Quantities m calculated in this way characterise interference rows but are burdened with errors caused by approximated values d and $n(\lambda)$, and generally are not integer (or half-integer) numbers. Therefore, one should try to use a few sets of values m to calculate, once again, the thickness d_2 (Tab. 3). The set of interference order numbers m that gives the smallest dispersion in d_2 should be taken into consideration to calculate the average value of the thickness from d_2 . This average value is assumed to be the real thickness of the polymer film.

A sequence of numbers m describing real interference orders and approximated to real thickness of polymer film — average value d_2 from Eq. (1) are used to

calculate refractive index n_2 as a function of wavelength λ . For the results obtained, the n_2 function in the form of Sellmeier equation

$$n^2 = A + \frac{B}{1 - C/\lambda^2} \quad (7)$$

was prepared to extrapolate to the domain of shorter wavelengths.

Based on the data collected in Table 3, the following equation for the dependence of refractive index n on wavelength λ was derived:

$$n^2 = -53.5931 + \frac{56.002}{1 - \frac{643.136}{\lambda^2}} \quad (8)$$

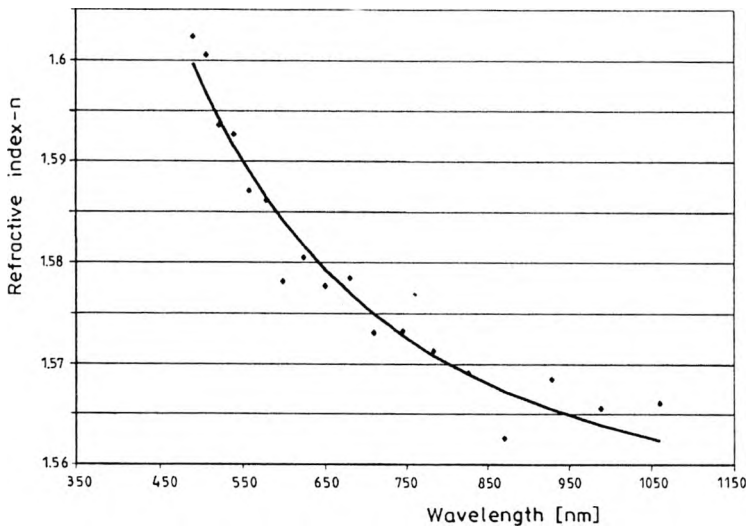


Fig. 4. Polymer Par 1-19 refractive index plotted against wavelength with a fitted curve calculated by Sellmeier's equation ($A = -53.5931$, $B = 56.002$, $C = 643.136$).

Measurement results T_s , T_m and T_M for each thin polymer film can be used to define average film thickness d and refractive index $n(\lambda)$, Fig. 4.

Determination of n , d , T_M and s values makes it possible to define absorption coefficient α of a polymer. The quantity x that is a quotient of transmitted intensity and incident intensity of beam can be written as follows [13]:

$$x = \frac{E_M - [E_M^2 - (n^2 - 1)^3 (n^2 - s^4)]^{1/2}}{(n - 1)^3 (n - s^2)} \quad (9)$$

where

$$E_M = \frac{8n^2s}{T_M} + (n^2 - 1)(n^2 - s^2). \quad (10)$$

Film absorption coefficient

$$\alpha = \frac{-\ln(x)}{d} \quad (11)$$

can be expressed as the imaginary part of the complex refractive index

$$n^* = n - ik \quad (12)$$

where

$$k = \frac{\alpha \lambda}{4\pi}, \quad (13)$$

n is a real part of refractive index.

The obtained values of complex refractive index $n^*(\lambda)$ can be used to calculate real χ_R and imaginary χ_I components of electric susceptibility for all polymers. Using well-known transformations one obtains:

$$\chi_R = n^2 - k^2 - 1, \quad \chi_I = 2nk \quad (14)$$

where χ_R are real and χ_I – imaginary susceptibility.

Finally, calculated quantities of refractive index $n(\lambda)$ may be substituted to Eq. (14) in order to find $\text{Re}\chi^{(1)}$.

4. Experimental results and conclusions

Based on the measurements of absorption the relation $s(\lambda)$ for glass (used for polymer films) was determined. Measurements results of multiple light beam reflections from substrate and polymer film for nine different polymer composites were used.

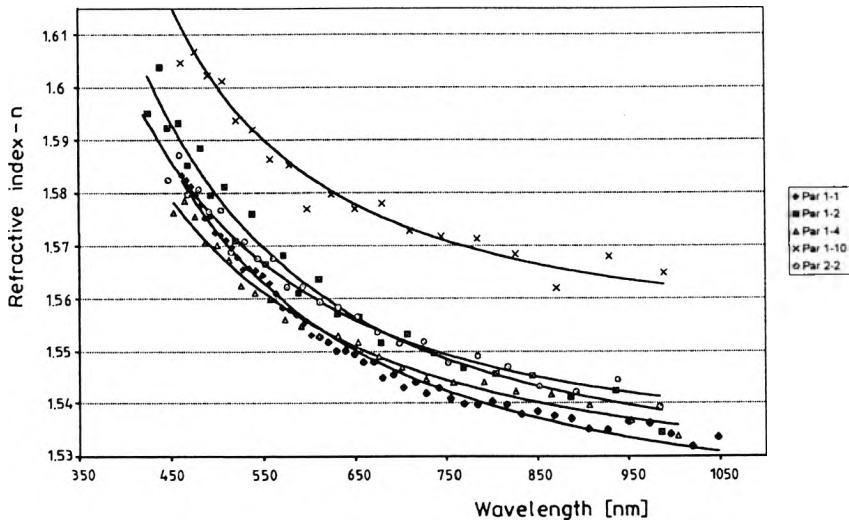


Fig. 5. Plot of refractive indices of polymers from the first main group PAR-1 (Par 1-1, Par 1-2, Par 1-4, Par 1-10, Par 2-2) as a function of wavelength with fitted Sellmeier's curves.

Table 4. Results of measurements.

Polymer Par:	Thickness d [nm]	Standard deviation of d [nm]	Fitted parameters: $n^2 = A + \frac{B}{1 - \frac{C}{\lambda^2}}$		
			A	B	C
1-1	6492	33.2	-0.2150	2.5230	15364
1-2	2731	22.7	0.1426	2.1835	17946.6822
1-4	2946	25	-58.1311	60.4561	561.4422
1-10	2370	15.1	1.91215	0.4983	57992.2449
2-2	3036	26.4	0.2441	2.0969	15559.2005
5-1	2554	13.7	-0.0369	2.4535	15158.8959
6-1	2758	14.4	0.1776	2.0408	14932.4846
6-2	2582	23.9	-0.0612	2.4383	15269.4769
7-1	2852	10.3	-0.4774	2.8932	15268.7519

The error elimination procedure makes it possible to determine n (Figs. 5 and 7) as a function of wavelength in the range from about 450 nm to 1000 nm (Tab. 4) for all the samples. The dependence of s on λ was used to determine the absorption α as a function of λ for compositions of all polymers (Figs. 6 and 8).

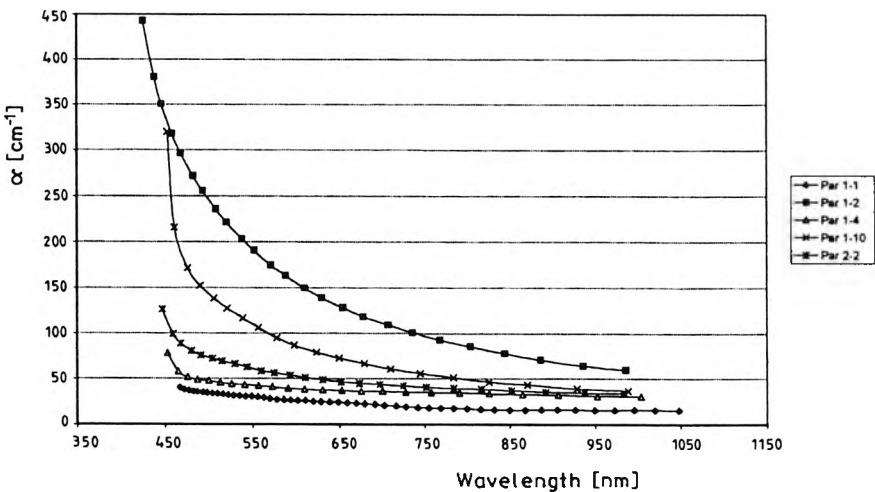


Fig. 6. Absorption of polymers from the first main group PAR-1 (Par 1-1, Par 1-2, Par 1-4, Par 1-10, Par 2-2) as a function of wavelength.

The accuracy of determination of the refractive index n as a function of wavelength for each polymer was improved (Tab. 5).

The results obtained were used to evaluate complex electric susceptibility $\chi^{(1)}$ (real and imaginary) components for each polymer composition (Tab. 5).

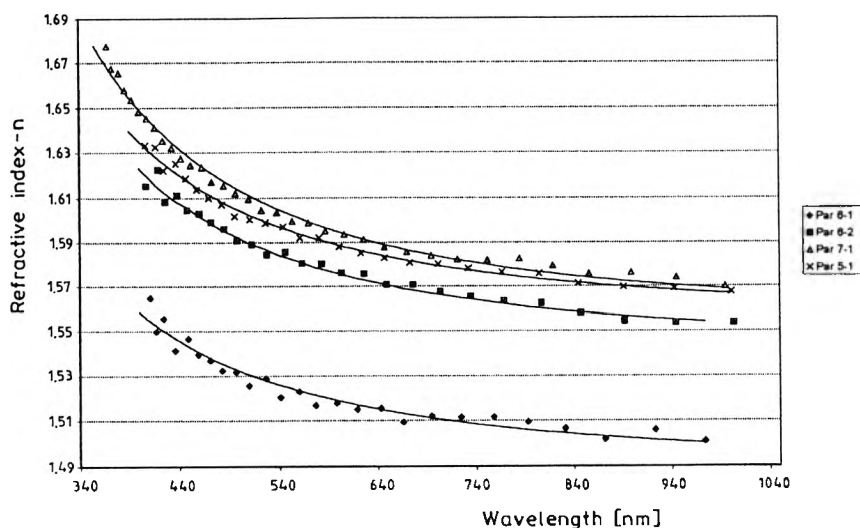


Fig. 7. Plot of refractive indices of polymers from the second main group PAR-2 (Par 6-1, Par 6-2, Par 7-1, Par 5-1) as a function of wavelength with fitted Sellmeier's curves.

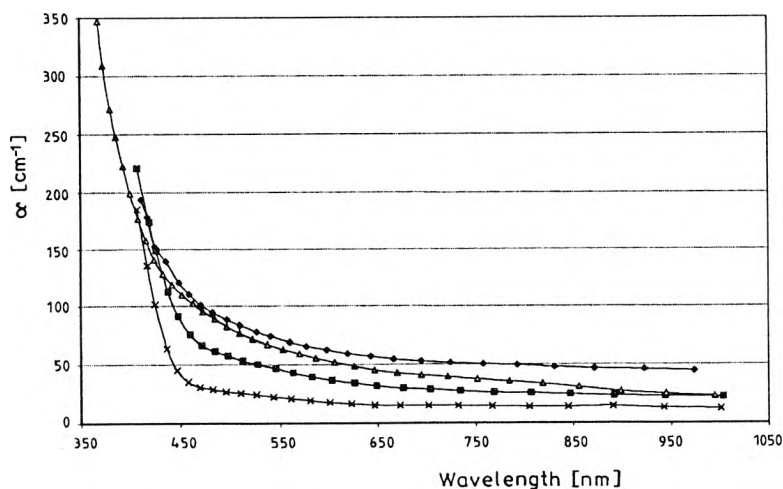


Fig. 8. Absorption of polymers from the second main group PAR-2 (Par 6-1, Par 6-2, Par 7-1, Par 5-1) as a function of wavelength.

The polymers investigated in this paper may be divided into two groups: PAR-1 and PAR-2 according to their chemical structure. There was no correlation between $n(\lambda)$, χ_R and chemical constitution of polymers. The PAR-1 polymers with largest refractive index like Par 1-10 strongly differ from other compositions. However, for polymers PAR-2 the largest refractive index exists for constitution with symbol Par 7-1. Values of residual polymer compounds of refractive indices $n(\lambda)$ are close to each other (Figs. 5 and 7).

Table 5. The calculated polymer susceptibilities.

No.	Polymer notation	Range of λ changes [nm]	Range of refractive index n changes	Range of Δn error changes	Range of α changes [cm^{-1}]	Range of $\Delta\alpha$ error changes [cm^{-1}]	Range of susceptibility χ_R changes	Susceptibility χ_I
1	Par 1-1	1048–462	1.5335–1.5834	0.006–0.0042	15.140–39.806	0.058–0.105	2.5498–1.4901	0.0006
2	Par 1-2	986–425	1.5345–1.5952	0.011–0.0092	59.280–442.944	0.425–2.554	3.0974–1.3929	0.0013
3	Par 1-4	1004–453	1.5338–1.5763	0.0109–0.0091	30.1376–78.326	0.213–0.451	2.8793–1.7179	0.0013
4	Par 1-10	989–453	1.5649–1.6247	0.0145–0.0149	36.175–319.992	0.338–2.935	1.4524–1.5664	0.0016
5	Par 2-2	984–447	1.5397–1.5825	0.0106–0.0092	33.578–126.325	0.230–0.733	2.8013–1.3880	0.0012
6	Par 5-1	1001–407	1.5675–1.6332	0.0099–0.0088	12.148–185.618	0.077–0.999	1.0383–1.6475	0.0013
7	Par 6-1	974–411	1.5010–1.5648	0.0104–0.009	44.616–194.052	0.308–1.115	1.6358–1.5731	0.0012
8	Par 6-2	1003–407	1.5535–1.5648	0.01–0.0091	22.148–221.019	0.142–1.284	3.2866–2.4392	0.0013
9	Par 7-1	995–368	1.5700–1.6778	0.0069–0.9955	22.913–347.034	0.101–1.138	2.8416–1.6896	0.0011

There was no big difference in absorption for polymers considered above. Though, polymer Par 1-2 shows a little bit better absorption for wavelength from 350 nm to 1100 nm.

References

- [1] POMPE G., LEHMACHER S., RUDOLPH S. *et al.*, Proc. SPIE **3281** (1998), 37.
- [2] NEYER A., KNOCHÉ T., MULLER L., Electron. Lett. **29** (1993), 399.
- [3] KRAGL H., HOHMANN R., MARHEINE C., *et al.*, Electron. Lett. **33** (1997), 2036.
- [4] KNOCHÉ T., MULLER L., KLEIN R., *et al.*, Electron. Lett. **32** (1996), 1285.
- [5] VOLODIN B.L., KIPPELN B., MEERHOLZ K., *et al.*, Opt. Lett. **21** (1996), 519.
- [6] WU J.W., J. Opt. Soc. Am. B **11** (1994), 8142.
- [7] VOLODIN B.L., KIPPELEN B., MEERHOLZ K., *et al.*, Opt. Soc. Am. B **13** (1996), 2261.
- [8] NONIEWICZ K., BRZOWSKI Z.K., ZADROŻNA I., J. Appl. Polymer Sci. **60** (1996), 1071.
- [9] BRZOWSKI Z.K., ZADROŻNA I., KOWALCZYK T., *et al.*, Polym. Polym. Compos. **3** (1995), 421.
- [10] ZADROŻNA I., BRZOWSKI Z.K., NONIEWICZ K., *et al.*, Polym. Polym. Compos. **5** (1997), 57.
- [11] BRZOWSKI Z.K., ZADROŻNA I., *Novel UV-sensitive polyarylates confirmed by NMR*, [In] XIII European Experimental NMR Conference, Paris, May 1996.
- [12] ZADROŻNA I., PARZUCHOWSKI P., BRZOWSKI Z.K., *et al.*, J. Appl. Polymer Sci. **71** (1999), 1017.
- [13] SWANEPOEL R., Phys. E: Sci. Instrum. **16** (1983), 1214.

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