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Polymers with a High Refractive Index and Low Optical Dispersion

By *Hans-U. Simmrock, Alfred Mathy, Ligia Dominguez, Wolfgang H. Meyer** and *Gerhard Wegner*

Materials for use in optics are usually characterized in terms of their refractive index n_D and their Abbe number ν_D which describes the wavelength dependence of the refractive index, the optical dispersion ($\nu_D = (n_D - 1)/(n_F - n_C)$ where n_D, n_F and n_C are the refractive numbers of the material at the wavelengths of the spectral lines of Na, F and C respectively).

In the n_D vs. ν_D diagram the regime of materials which combine high refractive indices with high Abbe numbers used to be exclusively occupied by inorganic glasses. Transparent polymers range from $n_D = 1.33$ to $n_D = 1.73$. However, polymers with high n_D values usually have low ν_D values and vice versa. For example, the data corresponding to two optically extreme polymers are: $n_D = 1.675$ and $\nu_D = 19$ for poly-*N*-vinylcarbazole and $n_D = 1.345$ and $\nu_D = 83$ for Teflon FEP (Fig. 1). Thus, the combination of high refractive index with low optical dispersion in polymers appeared until now to be unachievable.[1]

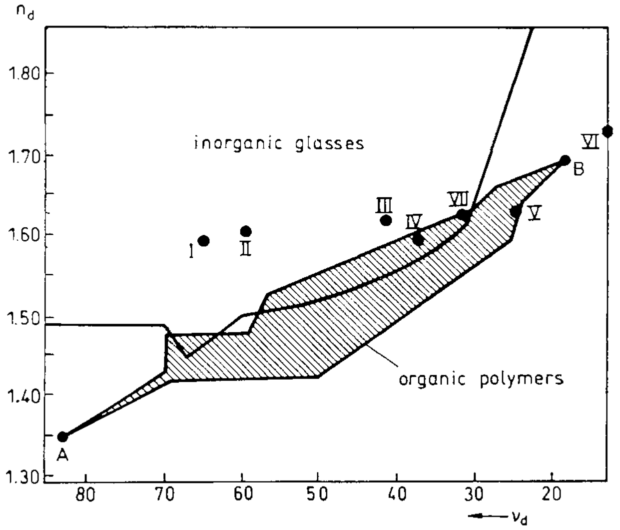

Fig. 1. Refractive indices and optical dispersion of ionenes and other materials: n_D vs. ν_D diagram. I, II, III, IV, V, VI and VII: Ionenes are defined in Table 1. A: Teflon FEP, B: Poly-*N*-vinylcarbazole.

Numerous efforts have been made in the past to extend the polymer regime towards higher indices and lower dispersion. We report here a successful approach using polyelectrolytes, in which the optical parameters can be adjusted by varying the structure of the polymer *and* by the proper choice of the counterions.[2] We use polyelectrolytes of the type **1**, which are also known as "Ionenes" (Io), with the main chain segments R^1, R^2 and the side chains R^3, R^4 being organic moieties (e.g. aliphatic groups), and X = monovalent (q = 1) or divalent (q = 0.5) counterions. The solid state properties of such polyelectrolytes are usually scorned as being "salt-like". Indeed, ionenes with R^1 and R^2 being relatively short aliphatic segments, due to their high charge density, are highly crystalline materials with physical and chemical properties resembling those of inorganic salts.[3]

1 $\left[R^1-\mathrm{N}(R^3)_2-R^2-\mathrm{N}(R^4)_2\right]_n\ 2\cdot n\cdot q\cdot X$

However, ionenes where R^1 and R^2 are larger organic components with low charge density have more polymer-like properties. They can be processed from the melt or from solution to form glassy films with excellent optical transmission in the visible and near-UV (Fig. 2). In such ionene glasses ionic conductivity has been recently demonstrated.[4]

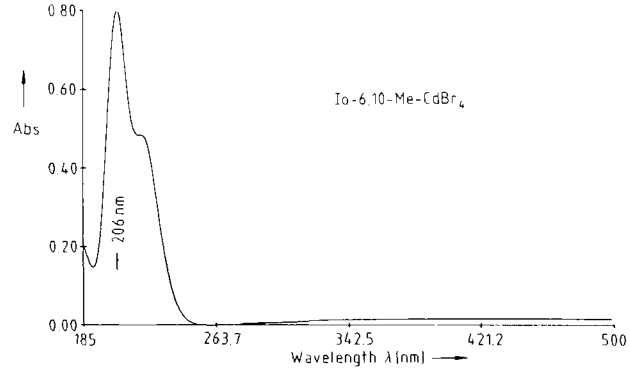

Fig. 2. UV-VIS-Absorption spectrum of a typical ionene-film (thickness: 1 μm; Io-6, 10-Me-CdBr$_4$ defined as in Table 1).

Recrystallization can be suppressed and long-term stability of the glassy state can be obtained by introducing a certain amount of irregularity along the polymeric structure such as in copolymers ($R^1 \neq R^2$) by using isomeric mixtures and by combining rigid and flexible chain segments. By these means the thermal behavior and the processibility of the materials can also be greatly influenced. For example: the glass transition temperature of Io-10-Et-BF$_4$ ($R^1 = R^2 = (CH_2)_{10}$; $R^3 = R^4 =$ ethyl; $X = BF_4$) is −22 °C, while that of Io-Do,Pip-Me-CdBr$_4$ ($R^1 = -CH_2-CH=CH-CH_2-$; $R^2 = -cyclo\text{-}NC_5H_9-(CH_2)_3-cyclo\text{-}C_5H_9N-$; $R^3 = R^4 =$ methyl; $X = CdBr_4$) is +191 °C. The thermal properties and relaxation phenomena in glassy ionenes have recently been discussed in detail elsewhere.[4]

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In contrast to ordinary polymers the counterions in polyelectrolytes provide an additional parameter by which the material properties can be influenced. With respect to the optical properties of ionenes the choice of counterion, turned out to be decisive: Due to the relatively simple structure of the polymer backbone a refractive index without counterions of only about 1.5 can be expected, while by the proper choice of X n_D can be shifted to 1.7 and higher.

Different counterions can be introduced into ionenes by metathetical ion exchange in solution following one of the experimental procedures described in detail elsewhere.[5] By these means materials with purities better than 99% with respect to the counterions can be obtained. Another possible method for counterion exchange in the glassy material are concentration or electrochemically driven diffusion processes.

For the optical measurements about 1 µm thick transparent films were obtained by spincoating from dimethylformamide (DMF) solutions. The optical parameters of the films were determined with a prism coupler as described in detail by *Ulrich* and *Torge*.[6, 7] The prism coupler can be used to determine the refractive index and the thickness of a light-guiding thin film. Both parameters can be obtained simultaneously and with good accuracy (n_D better than ± 0.0005) by measuring the coupling angles at the prism and fitting them to a theoretical dispersion curve. Using laser light of different wavelengths, the wavelength dependence of the refractive index and thus the Abbe-numbers can also be determined.

Table 1. Chemical structures and optical properties of selected ionenes.

No. [a]	Ionene	R^1 [b]	R^2 [b]	R^3 [b]	R^4 [b]	X [b]	n_D	ν_D
I	Io-Do,10-Me-$ZnBr_4$	$CH_2-CH=CH-CH_2$	$(CH_2)_{10}$	CH_3	CH_3	$ZnBr_4$	1.5911	65.0
II	Io-Do,Pip-Me-$CdBr_4$	$CH_2-CH=CH-CH_2$	*cyclo*-$NC_5H_9-(CH_2)_3-$ *cyclo*-C_5H_9N	CH_3	[c]	$CdBr_4$	1.6018	59.7
III	Io-Do,Pip-Me-BPh_4	$CH_2-CH=CH-CH_2$	*cyclo*-$NC_5H_9-(CH_2)_3-$ *cyclo*-C_5H_9N	CH_3	[c]	BPh_4	1.6142	41.0
IV	Io-6,10-Me-$CdBr_4$	$(CH_2)_6$	$(CH_2)_{10}$	CH_3	CH_3	$CdBr_4$	1.5858	37.6
V	Io-6,10-Me-CdI_2Br_2	$(CH_2)_6$	$(CH_2)_{10}$	CH_3	CH_3	CdI_2Br_2	1.6250	24.6
VI	Io-6,Do-Et-HgI_4	$CH_2-CH=CH-CH_2$	$(CH_2)_6$	CH_2CH_3	CH_2CH_3	HgI_4	1.7245	13.2
VII	Io-6,10-Me-ZnI_2Br_2	$(CH_2)_6$	$(CH_2)_{10}$	CH_3	CH_3	ZnI_2Br_2	1.6260	31.6

[a] Numbers corresponding to Fig. 1. [b] Defined as in structure 1. [c] Due to cyclic structure only one CH_3 group.

The optical parameters of a selection of different ionenes are compiled in Table 1 and displayed in Figure 1.

Obviously, with refractive indices between 1.58 and 1.72 and Abbe-numbers up to 65 the ionenes have intruded into the regime of inorganic glasses. When comparing ionenes with polymers with identical backbone structures but different counterions the influence of the polarizability of X on the refractive index can be substantiated: e.g. Io-6,10-Me-$CdBr_4$ exhibits an $n_D = 1.5858$, while the corresponding ionene combined with the more polarizable CdI_2Br_2 exhibits an $n_D = 1.6250$.

Similarly, the absorption of the counterions plays a rôle in the dispersion: a couterion absorbing in the UV such as $CdBr_4$ gives rise to a relatively low dispersion, whereas a counterion absorbing closer to the visible such as CdI_2Br_2 gives rise to a higher dispersion.

With the determination of the optical parameters by the prism coupler method the applicability of polyelectrolyte glasses as waveguiding material has been demonstrated. Since the choices are so manifold for the backbone structures and the counterions, a great variety of materials with tailor-made optical and other physical as well as chemical properties can be made. Therefore, the application of this class of materials in optics appears to be very promising.

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In future issues, regular series will be run in the Research News section on Biomaterials (G. Heimke), Interfaces and Joining (G. Partridge), Surface Analysis (J. Rabe), Diamond Films (P. Bachmann) and Polymers (M. Ballauff) amongst others. Further contributions on any new developments in materials science are welcome, the articles (4–5 pages manuscript plus 1 or 2 figures) being assessed by the Editorial Advisors and the Editorial Staff. Manuscripts should be sent to ADVANCED MATERIALS P.O. Box 101161 D-6940 Weinheim, FRG.