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What Is the Lowest Refractive Index of an Organic Polymer?

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ABSTRACT: The refractive index is a key feature in the application of optical polymers. The continuous development of new materials for technological fields such as optical fibers or lenses poses the question about the fundamental physical limits of this class of materials. By using the Lorenz–Lorentz equation, we have investigated the theoretical lower limit of the refractive index of organic polymers. Starting from an extended data base, we have evaluated optimized refractive and density increments for functional groups. Using a "construction plan" for low-index polymers, we expect the lower limit to be close to 1.29. To our knowledge this is the first estimate of this fundamental limit.

1. Introduction

One of the key features of organic polymers used in optical applications is the refractive index. Lenses, optical waveguides, and nonlinear optical devices are just three examples where this material parameter plays a key role in the system design.

A special area where the refractive index has to be matched carefully is the preparation of polymer optical fibers.[1,3] The numerical aperture of the fiber NA is determined by the refractive index of the core (n_1) and cladding (n_2) materials

$$\mathrm{NA} = (n_1^{\,2} - n_2^{\,2})^{1/2} \qquad (1)$$

and affects important fiber properties like pulse dispersion and the amount of power coupled into the fiber from a light emitter.

Efforts to lower the fiber attenuation focus on the use of deuterated or fluorinated core polymers.[1,4,5] In the latter case, the refractive index is lower compared to that of its deuterated or hydrogenated counterpart. For polymers with a high degree of fluorination, i.e., refractive indices of 1.35–1.37, it is increasingly difficult to find a cladding polymer with an index as low as 1.30–1.32 to maintain a reasonable numerical aperture. For longer distance applications even larger NAs might be preferred, resulting in a demand for lower cladding refractive indices in the range of 1.25–1.28. Here, the questions arise if such polymers can exist and what their preferred molecular structures are.

In view of the above-mentioned applications of low-index polymers, we consider thermoplastic polymers rather than "noncompact" materials such as aerogels.

In a detailed literature study we found the refractive index n_D (λ = 589 nm) for several fluoropolymers to lie between 1.36 and 1.38. Dislich[6] proposed a lower limit of about 1.33. However, this is an estimate from a screening of published polymer data existing at that time rather than a substantiated physical limit, such as we present in this paper.

We also made estimates using an incremental model based on the well-known Lorenz–Lorentz equation and the refractive increments published for a number of atoms[7] and chemical groups. We found that for identical increments the values given in different sources deviate significantly. In addition, there is no "construction plan" available for polymer molecules to guarantee lowest refractive index.

These two shortcomings have been addressed by the following procedures:

1. To improve the molar refractive increments for various chemical groups, we extracted over 60 polymers from the literature with their respective densities and experimental n_D values. Data for a set of fluoropolymers were added from our own measurements. The polymer repeating units were then separated into individual groups, each of them being assigned a refractive index increment. According to the Lorenz–Lorentz formalism, these increments together with the polymer density and the molecular weight of the repeating unit determine the polymer refractive index. In writing these equations for all polymers, we get a system of linear equations with the group refractive increments as variables. Due to the large number of equations and the limited number of individual increments, this system of equations is overdetermined and can be solved, resulting in optimized group refractive increments. Only these increments are subsequently used for further considerations. A similar procedure has been applied to the molar volumes of individual increments. Details of the mathematical procedure are given in Section 3.

2. As a "construction plan" for low refractive index polymers, we used the following guideline: In the simplest case an organic polymer consists of a C–C main chain. The substituents on the C atoms can be either single atoms or groups, e.g., to form a side chain. To end up with a low refractive index polymer, the ratio of molar refraction and the required volume of an individual substituent must be kept as low as possible. How to select the right substituents is described in the next section.

2. Refractive Index Contribution of Individual Atoms

A material with a low refractive index has to have a low polarizability; i.e., the dipole moment per unit volume induced by the electromagnetic field has to be minimal. In Figure 1 we have plotted the ratio of molar refraction R_L (proportional to the induced dipole moment) to molar volume V_L for different atoms present in organic polymers.[8-10] As one might expect, there is a broad range of values for each atom due to different binding structures and a varying chemical environment in different organic or inorganic compounds. However, it can be seen that fluorine and, to a smaller degree, oxygen lower the refractive index of a compound, whereas nitrogen, sulfur, and the heavier halogens have higher ratios and thus should not be present in a low refractive index polymer.

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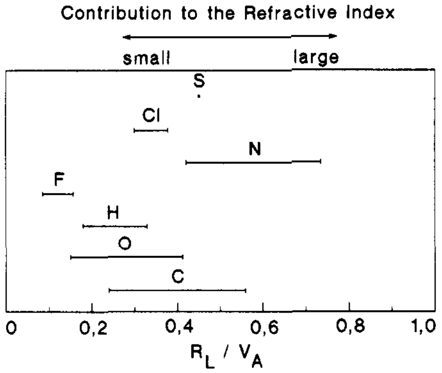


Figure 1. Contribution of different atoms to the refractive index of a compound.

Table I
Increments of Various Polymer Substructures

no.	increment	R_j	ΔR_j	V_j	ΔV_j	x	Δx
1	CF_3	6.149	±0.66	40.274	±2.78	0.153	±0.020
2	CF_2CF_3	11.209	±1.00	67.913	±4.19	0.165	±0.018
3	$CF(CF_3)_2$	15.782	±1.18	93.013	±4.94	0.170	±0.016
4	$CH(CF_3)_2$	15.710	±1.12	88.633	±4.72	0.177	±0.016
5	O (ether)	1.625	±0.68	9.052	±2.86	0.180	±0.094
6	OCF_2O	8.311	±1.22	45.743	±5.11	0.182	±0.033
7	OCF_2CF_2	11.747	±1.25	64.331	±5.27	0.183	±0.025
8	CF_2	5.061	±0.75	27.640	±3.13	0.183	±0.034
9	CF_2H	5.729	±1.10	29.616	±4.62	0.194	±0.048
10	CO_3	6.266	±1.07	31.608	±4.50	0.198	±0.044
11	$CO_2CH(CF_3)_2$	21.998	±1.16	111.394	±4.86	0.198	±0.014
12	CCF_3	8.123	±1.38	37.121	±5.81	0.218	±0.051
13	CH_3	5.901	±0.59	25.798	±2.50	0.229	±0.032
14	OCH_2O	7.754	±0.96	33.631	±4.06	0.231	±0.040
15	CO_2CH_3	12.189	±0.66	48.559	±2.77	0.251	±0.020
16	CH_2CH_3	10.404	±0.60	41.326	±2.52	0.252	±0.021
17	CN	6.477	±0.74	24.445	±3.12	0.265	±0.046
18	CH_2O	6.312	±0.40	23.648	±1.68	0.270	±0.025
19	CO_2	6.289	±0.28	22.761	±1.19	0.276	±0.019
20	C_6F_5 (arom)	27.181	±0.94	97.645	±3.93	0.278	±0.015
21	CF	3.485	±0.72	12.466	±3.01	0.280	±0.089
22	CHOH	5.851	±0.69	20.288	±2.90	0.288	±0.054
23	CH_2	4.504	±0.08	15.528	±0.35	0.290	±0.008
24	CHO	5.158	±0.36	17.078	±1.53	0.302	±0.035
25	CHF	4.082	±1.05	13.460	±4.40	0.303	±0.126
26	CCl_3	20.620	±0.77	67.096	±3.23	0.307	±0.019
27	CFCl	10.450	±1.01	33.022	±4.26	0.317	±0.051
28	CHCl	9.633	±0.69	29.598	±2.90	0.326	±0.040
29	CCH_3	7.875	±1.35	22.645	±5.68	0.347	±0.106
30	SO_2	9.630	±1.23	27.713	±5.15	0.348	±0.078
31	C_6H_5 (arom)	25.824	±0.69	74.129	±2.90	0.348	±0.011
32	C=O	4.590	±0.71	13.170	±2.97	0.349	±0.095
33	Br	10.116	±1.02	28.843	±4.27	0.351	±0.063
34	C_6Cl_5 (arom)	51.454	±0.81	140.399	±3.40	0.367	±0.011
35	CCl_2	15.786	±0.69	41.498	±2.90	0.380	±0.031
36	CONH	8.256	±0.56	21.660	±2.34	0.381	±0.049
37	*p*-C_6H_4 (arom)	25.235	±0.38	65.912	±1.61	0.383	±0.011
38	CH	3.412	±0.62	8.085	±2.61	0.422	±0.032
39	C_6H_3 (arom)	24.785	±1.04	53.710	±4.37	0.462	±0.042

3. Mathematical Procedure To Evaluate Optimized Refractive and Volume Increments

The Lorenz–Lorentz equation (2) offers the possibility to calculate the refractive index n_D of an unknown polymer, if its molar refraction R_L and density ρ are known:[10]

$$\frac{n_D^2 - 1}{n_D^2 + 2}\frac{M_G}{\rho} = R_L = \sum_{j=1}^{J} k_j R_j \tag{2}$$

where n_D is the refractive index, M_G is the molecular weight of the repeating unit, ρ is the density (g/cm^3), R_L is the molar refraction (cm^3/mol), k_j is the number of increments of the substructure j in the repeating unit, R_j is the molar refraction increment of substructure j (cm^3/mol), and J is the total number of individual substructures. According to eq 2 the molar refraction R_L can be regarded as a sum of refraction increments R_j, each corresponding to a particular functional group within the polymer repeating unit. This is illustrated for poly(methyl methacrylate) (PMMA) in the following example:

substructure	R_j
CH_2	4.504
CCH_3	7.875
CO_2	6.289
CH_3	5.901
	R_L = 24.569

The incremental values are taken from Table I. Together with the density of $\rho = 1.15$ g/cm^3 this results in a refractive index of $n_D = 1.478$, which is in very good agreement with the experimental value of 1.489.[11]

With

$$\rho/M_G = V_L \tag{3}$$

the molar volume V_L can be expressed in the same way as the molar refraction:

$$\rho/M_G = \sum_{j=1}^{J} k_j V_j \tag{4}$$

For a given polymer, we now can write an equation for the molar refraction according to eq 2 and for the molar volume according to eq 4. For a large number of polymers (63 in our case) this results in a system of linear equations. The polymers were properly selected[12-14] so that the total number of different increments is much lower than the number of equations, resulting in an overdetermined system.

By using a root-mean-square procedure, the refraction and volume increments R_j and V_j, respectively, were optimized:

$$\sum_{i=1}^{I} (R_{L_i} - R_{L_i}{}^*)^2 \Rightarrow \text{minimum} \tag{5a}$$

$$\sum_{i=1}^{I} (V_{L_i} - V_{L_i}{}^*)^2 \Rightarrow \text{minimum} \tag{5b}$$

where $R_{L_i}{}^*$ and $V_{L_i}{}^*$ are experimental values obtained by using measured n_D, ρ, and R_{L_i} and V_{L_i} are calculated values; and I is the total number of equations (polymers).

It is obvious that the quality of the optimization is directly correlated with the number and precision of the input data. However, reliable and complete sets of data for the refractive index and the density are only available for a small number of amorphous polymers, so our own data, especially on fluoropolymers, have been added.

As mentioned before, the quotient

$$x = R_j/V_j \tag{6}$$

is the contribution of each increment to the resulting refractive index. The corresponding error Δx is given by

$$\Delta x = \left[\left(\Delta R_j \frac{1}{V_j}\right)^2 + \left(\Delta V_j \frac{-R_j}{V_j^2}\right)^2\right]^{1/2} \tag{7}$$

Using eq 2, the refractive index n_D is given by

$$n_D = \left[\frac{1 + 2R_L\frac{\rho}{M_G}}{1 - R_L\frac{\rho}{M_G}}\right]^{1/2} = \left[\frac{1 + 2\frac{R_L}{V_L}}{1 - \frac{R_L}{V_L}}\right]^{1/2} \tag{8}$$

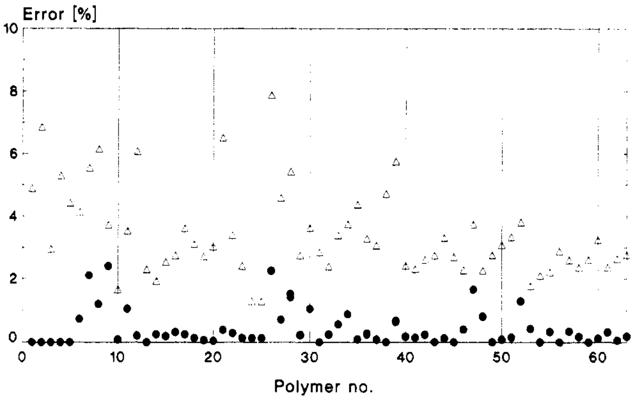


Figure 2. Errors of the refractive index. "△" marks the errors, calculated by the error propagation method (eq 9); "●" marks the deviation between calculated and experimental values.

The corresponding uncertainty Δn_D, which is caused by errors in the calculated R_L and V_L, is

$$\Delta n_D = \left[\left(\Delta R_L \frac{\partial n_D}{\partial R_L}\right)^2 + \left(\Delta V_L \frac{\partial n_D}{\partial V_L}\right)^2\right]^{1/2} \tag{9}$$

with

$$\Delta R_L = [\sum_{j=1}^{J} k_j (\Delta R_j)^2]^{1/2} \tag{10a}$$

$$\Delta V_L = [\sum_{j=1}^{J} k_j (\Delta V_j)^2]^{1/2} \tag{10b}$$

and

$$\frac{\partial n_D}{\partial R_L} = \frac{3V_L}{2n_D} \frac{1}{(V_L - R_L)^2} \tag{11a}$$

$$\frac{\partial n_D}{\partial V_L} = -\frac{3R_L}{2n_D} \frac{1}{(V_L - R_L)^2} \tag{11b}$$

In Figure 2, we have plotted the calculated errors according to eq 9 together with the deviations between calculated and experimental refractive indices. As can be seen, the calculated n_D values fit well with the experimental data. The estimated error can be regarded as an upper limit for the deviation.

4. Results and Discussion

The results of the calculations for various substructures are shown in Table I. For further considerations we have also added some increments which are composed of two or more substructures calculated by the optimization procedure.

With the optimized increments given in columns 3 and 4, we now can calculate the ratio $x = R_j/V_j$ for a variety of functional groups and fragments. It is important to note that these values are a direct measure of the refractive index contribution of that particular group in an *amorphous organic polymer below the glass transition temperature*. These numbers are given in column 5 and are arranged by increasing values.

As was expected from Figure 1, functional groups with a high fluorine content, like CF_3 and CF_2, have the lowest refractive index contribution. Therefore, these are preferred structural elements for low refractive index polymers. The value for the ether group (increment 5 in Table I) is also remarkably low. The reason for that is the relatively large volume occupied by the oxygen in this binding structure. On the other hand, the large values for the carbonyl and carboxyl groups, respectively, make carbon esters unsuitable for low-index polymers.

Table II
Increments for Polymer Main Chains[a]

no.	polymer main chain[b]	R_j	ΔR_j	V_j	ΔV_j	x	Δx
1	$-(CF_2C^*F_2)-$	10.121	±1.05	25.279	±4.43	0.183	±0.034
2	$-(CF_2C^*(CF_3))-$	13.183	±1.57	64.761	±6.60	0.204	±0.032
3	$-(CF_2C^*F)-$	8.546	±1.03	40.105	±4.34	0.213	±0.035
4	$-(C^*FC^*F)-$	6.970	±1.01	24.931	±4.25	0.280	±0.089
5	$-(CH_2C^*F)-$	7.989	±0.72	27.993	±3.03	0.285	±0.040
6	$-(CH_2C^*(CH_3))-$	12.378	±1.35	38.173	±5.70	0.324	±0.060
7	$-(CH_2C^*H)-$	7.915	±0.63	23.613	±2.64	0.335	±0.046

[a] To calculate the error Δx for polymers 1 and 4, the repeating unit was reduced to the smallest periodic substructure, CF_2 and CF, respectively. [b] Asterisks indicate positions at which a side chain may be added.

Table III
Polymers with Low Refractive Index

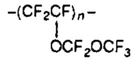
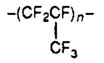
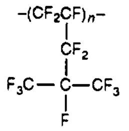
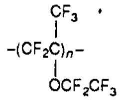
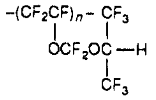
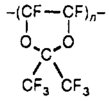
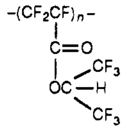
no.	polymer structure	R_L/V_L	calcd refractive index n_D
1		0.182 ± 0.017	1.292 ± 0.030
2		0.183 ± 0.019	1.293 ± 0.033
3		0.183 ± 0.014	1.293 ± 0.037
4		0.184 ± 0.018	1.294 ± 0.037
5		0.187 ± 0.014	1.299 ± 0.029
6		0.203 ± 0.023	1.329 ± 0.047
7		0.215 ± 0.013	1.350 ± 0.033

Table II gives a selection of polymer main chains, arranged according to their refractive index contribution.

From all possible organic fluoropolymers structures 2 and 3 contribute least to the refractive index, because they are composed of the lowest contributing structures in Table I. Although the $-(CF_2CF_2)-$ chain is still lower, it can form only a single polymer, i.e., the crystalline poly(tetrafluoroethylene) (PTFE) with a relatively high refractive index of 1.35 due to the higher density of the crystallites (the calculated refractive index of an "amorphous" PTFE is $n_D = 1.293$).

From a theoretical point of view the ideal molecular structure for an amorphous polymer with minimum refractive index consists of trifluoroethylene or (trifluoromethyl)difluoroethylene units as the main chain and CF_3, CF_2, or corresponding ether groups as the side chain. To inhibit crystallization, either homopolymers with branched side chains or copolymers, e.g., with tetrafluoroethylene, are most preferred.

Following this construction plan, Table III shows selected examples of low refractive index polymers. The indicated structures are based on theoretical considerations and are not checked for "practical" aspects such as monomer synthesizability or tendency to polymerize.

The second column in Table III gives the ratio of molar refraction to molar volume, where both values represent total values for the repeating unit, i.e., are sums over the respective values for the functional groups. In the third column we have calculated the refractive index using eq 8. The indicated uncertainty interval is given by eq 9. As can be seen, the lowest refractive indices are in the range of 1.29 with an uncertainty of ±0.03. This is the theoretical lower limit for an amorphous organic polymer.

In view of the good agreement between experiment and calculation (Figure 2), we feel that the actual lower limit is probably very close to 1.29.

The polymer with the lowest refractive index we are aware of is Teflon AF (registered trade mark of E. I. du Pont de Nemours), an amorphous fluoropolymer. Values are reported in the range of 1.29–1.31.[15] According to the aforementioned calculations, this polymer has to be composed mainly of CF, CF_2, and CF_3 groups and its refractive index is very close to the theoretical lower limit.

5. Conclusion

In conclusion we can make the following general statements about the influence of various functional groups on the refractive index:

Very low refractive polymers can be obtained by (exclusively) using the following structural elements: CF_3, OCF_2O, CF_2, $CF(CF_3)_2$, and $CH(CF_3)_2$.

The best-suited main chains are $-(CF_2C^*CF_3)-$, $-(CF_2C^*F)-$, and $-(C^*FC^*F)-$.

The best-suited side chains are CF_3, CF_2CF_3, $CF(CF_3)_2$, $CH(CF_3)_2$.

H atoms should be avoided in favor of fluorine.

Monomers should not contain S, N, Cl, Br, or I.

Monomers should not contain carbonyl or carboxyl groups.

To inhibit crystallization, i.e., generation of higher density segments which increase the refractive index, copolymerization (e.g., with tetrafluoroethylene) should be considered.

The theoretical lower limit of the refractive index of organic polymers is expected to be 1.26–1.29, probably very close to 1.29.

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