

Chimia 47 (1993) 397
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 ISSN 0009-4293

Optical Components

Joachim H. Wendorff*

Organic polymers have the distinct advantage that they can easily be processed into complicated three-dimensional parts, thin films or fibers, thin coatings on substrates. Moulding in the molten state, spin-coating from solution or casting from solution are just some of the possible

processing methods. Polymers are thus extremely well suited for the manufacturing of optical components, particularly for optical communications. Polymers possess the additional advantage that the relation between their chemical structure and relevant optical properties (refractive in-

dex, birefringence, absorption, nonlinear optical properties) is rather transparent and can in many instances already be predicted by molecular modeling techniques. This contribution describes the use of polymers in optical components, taking as examples amorphous polymers as well as liquid crystalline polymers. It also addresses a set of problems related to the organic nature of the polymers such as dimensional instability, chemical degradation, water uptake, physical aging.

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Effect of Structure on the Scattering Losses of Polymer Optical Fibre Materials

Manfred Dettenmaier*

Abstract. Since scattering of light, together with absorption, contributes to the total loss in optical fibres, it is important to study the scattering behaviour of polymers as a function of their molecular and supramolecular structure. Light-scattering of glassy homopolymers results from anisotropy and density fluctuations. The two contributions have been studied in detail. Particular attention has been given to long-range density fluctuations which depend on the thermal history of the material. Glassy polymer mixtures and copolymers exhibit additional scattering from concentration fluctuations. This contribution has been estimated theoretically. Experiments conducted on a semicrystalline polymer indicate that transformation of a spherulitic into a fibre morphology is an interesting method to reduce the scattering loss of melt-crystallized polymers.

1. Introduction

Optical fibres for long-distance data transmission are manufactured from highly purified inorganic glasses which exhibit much lower losses (≤ 0.5 dB/km) than polymer fibres (≥ 100 dB/km). For data transmission over shorter distances, however, polymer optical fibres represent a low-cost alternative with better mechani-

cal properties and less complex engineering solutions to the problem of fibre connection. Polymer optical fibres are likely to find diverse applications as local area networks, short data links, light pipes for automotive dashboard displays, etc. Since scattering of light, together with absorption, contributes to the total loss in optical fibres, it is important to study the scattering behaviour of polymers as a function of their molecular and supramolecular structure. Scattering of light results from fluctuations of the refractive index which may be caused by anisotropy, density and concentration fluctuations. The amount and

angular dependence of the scattered light are governed by the amplitude and correlation length of these fluctuations, respectively. The scattering loss is obtained by integration of the intensity over the whole angular range. In order to fully exploit the great potential of polymer optical fibres, interest has been focused on the scattering behaviour of such diverse systems as glassy homopolymers, polymer mixtures, and copolymers, as well as semicrystalline polymer fibres. The information obtained from the theoretical and experimental studies may be used to improve specific physical properties of future core and cladding materials while keeping their scattering losses acceptable.

2. General Considerations

Fig. 1 shows the structure of an optical fibre in which light propagates by total reflection at the core-cladding interface. The attenuation of light along the fibre is given by the equation

$$I = I_0 e^{-\sigma l} \quad (1)$$

where

I_0 = intensity of incident light

I = intensity of light after propagating a distance l

σ = attenuation coefficient

Instead of σ , the loss coefficient

$$\alpha = -\frac{1}{l} 10 \log_{10} \frac{I}{I_0} = 4.343 \sigma \quad (2)$$

is frequently used to express the loss of the fibre in units of dB/km.

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In the absence of impurities and defects, attenuation of light results from absorption and scattering of the fibre materials. This article concentrates on the second contribution which is intimately related to the structure of the materials.

3. Glassy Polymers

3.1. Homopolymers

Considerable interest has been focused on the scattering behaviour of glassy homopolymers such as poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate (PC) [1-7]. From these studies, it is well known that both anisotropy and density fluctuations of the refractive index contribute to the total amount of light scattering. The two contributions may be separated by measuring the scattering components for different polarization directions of the incident and scattered light. The scattering components of an unoriented amorphous polymer exhibit spherical symmetry, *i.e.* they are only a function of the magnitude of the scattering vector

$$s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (3)$$

where λ designates the wavelength of light in the material, and θ is the angle between the wave vectors of the incident and scattered waves. Because of the spherical symmetry the scattering components are measured in a single plane. The scattering components X_Y expressed as *Rayleigh* ratios refer to the directions of the analyzer (X) and polarizer (Y) which are oriented vertical (X, Y = V) or horizontal (X, Y = H) to the scattering plane. Since

$$V_H = H_V \quad (4)$$

and

$$H_H = V_V \cos^2 \theta + H_V \sin^2 \theta \quad (5)$$

measurements of only two components, *e.g.* V_V and V_H , are sufficient to characterize the scattering behaviour. The depolarized light-scattering component V_H results from anisotropy fluctuations of the

refractive index. The component V_V for incident and scattered waves having the same polarization direction may be written in the form

$$V_V = V_V^D + \frac{4}{3} V_H \quad (6)$$

where the first and second term represent the contributions from density and anisotropy fluctuations, respectively.

The attenuation coefficient for scattering is obtained by integration of the scattering components over the whole angular range

$$\sigma = \pi \int_0^\pi (V_V + V_H + H_V + H_H) \sin \theta d\theta \quad (7)$$

With Eqns. 4-6, σ may be written in the form

$$\sigma = \sigma^D + \sigma^A \quad (8)$$

where

$$\sigma^D = \pi \int_0^\pi V_V^D (1 + \cos^2 \theta) \sin \theta d\theta \quad (9)$$

and

$$\sigma^A = \pi \int_0^\pi V_V^D (1 + \cos^2 \theta) \sin \theta d\theta \quad (9)$$

are the contributions from density and anisotropy fluctuations, respectively. The loss coefficient defined in Eqn. 2 may be written in an analogous form

$$\alpha = \alpha^D + \alpha^A \quad (11)$$

using Eqns. 8-10

Studies on PMMA, PS, and PC have shown that V_H is independent of the scattering angle, *i.e.* $V_H(s) = \text{const}$. This result indicates that the anisotropy fluctuations of the refractive index extend over regions small compared to the wavelength of light. The magnitude of V_H , and hence α^A , is governed by the optical anisotropy of the monomer unit and intramolecular chain correlations [3]. PMMA is the core material that is most frequently used in polymer optical fibres. Since the monomer unit is nearly isotropic α^A is small as shown in the Table.

The angular dependence of the V_V^D component clearly reveals the existence of long-range density fluctuations in both amorphous polymers [1-7] and glass forming liquids of low molecular weight [8]. These fluctuations may be described by a

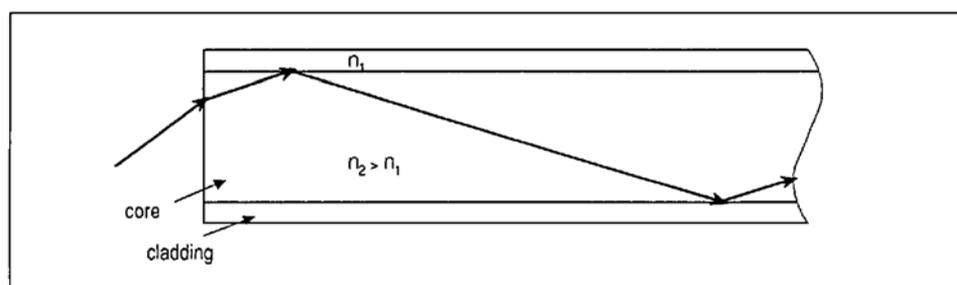


Fig. 1. Structure of an optical fibre with refractive indices of the cladding and core materials n_1 and n_2 , respectively

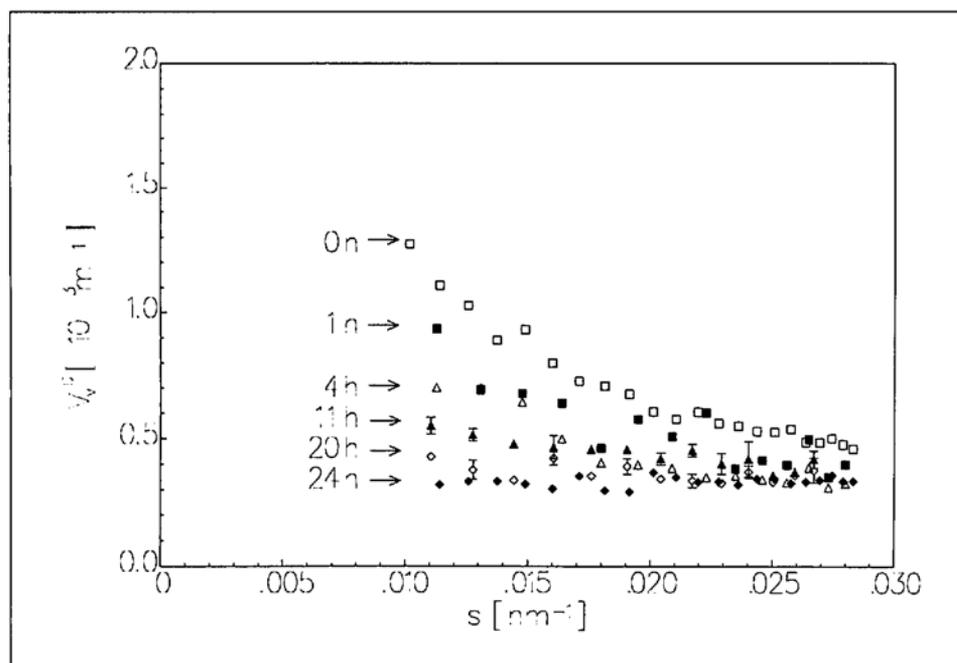


Fig. 2. V_V^D Component of light-scattering from density fluctuations in poly(methyl methacrylate) vs. magnitude of the scattering vector. Parameter is the annealing time of the samples at $T = 180^\circ$.

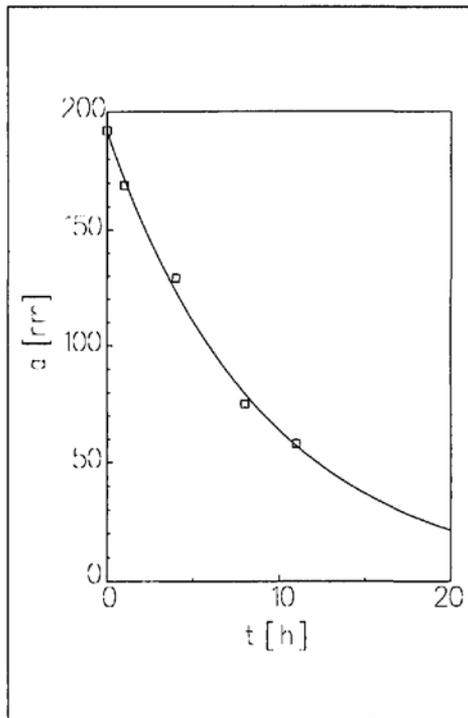


Fig. 3. Correlation length as a function of time for poly(methyl methacrylate) annealed at T = 180°

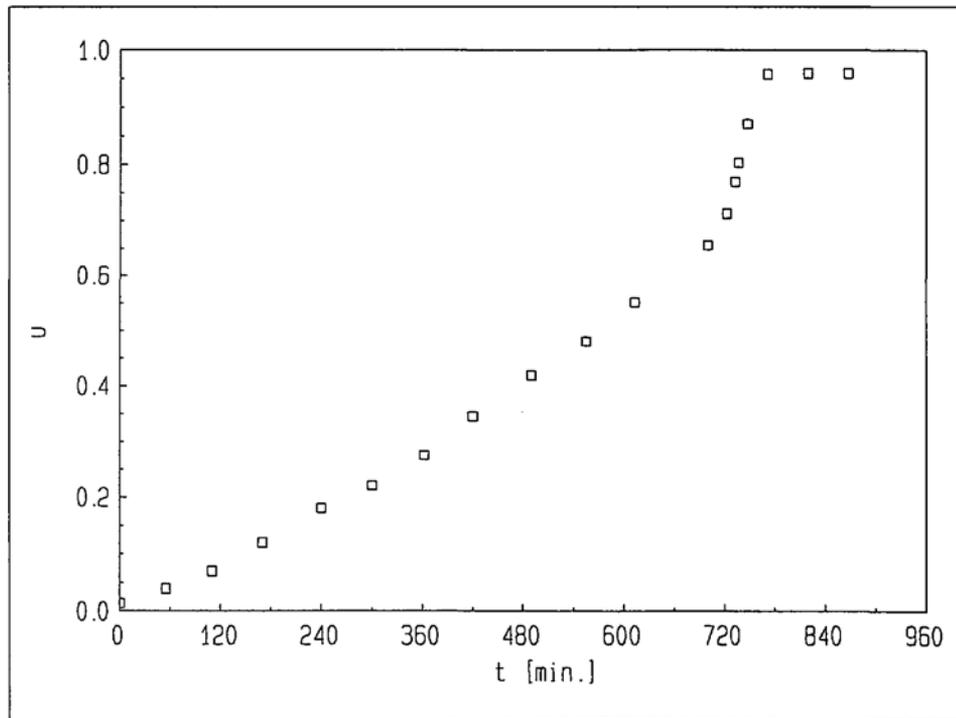


Fig. 4. Conversion as a function of time for methyl methacrylate polymerized at T = 90°

correlation function $F(r)$ which is related to V_V^D by a Fourier transformation

$$V_V^D(s) = \frac{16 \pi^3}{\lambda_0^4} n^2 \langle \Delta n^2 \rangle \int_0^\infty F(r) r^2 \frac{\sin(rs)}{rs} dr \quad (12)$$

λ_0 = wavelength of light in vacuum
 n = refractive index
 $\langle \Delta n^2 \rangle$ = mean square fluctuation of the refractive index.

Correlation functions derived by Debye and Bueche [9]

$$F(r) = e^{-\frac{r}{a}} \quad (13)$$

as well as by Ornstein and Zernicke [10]

$$F(r) = \frac{\Delta}{r} e^{-\frac{r}{a}} \quad (14)$$

have been used to describe the scattering data [1-4][6-8]. The thermal history of the glass forming system strongly affects the long-range density fluctuations [6-8]. This is shown in Figs. 2 and 3 for PMMA samples annealed at T = 180° ($T_g = 120^\circ$). The V_V^D Component (Fig. 2) and the correlation length a (Fig. 3) evaluated from Eqns. 12 and 14 decrease with increasing annealing time. The origin of the long-range density fluctuations is presently not very well understood. However, there is strong evidence that they are closely related to the glass transition [7][8]. For example, Figs. 4 and 5 show that the V_V component of polymerizing MMA becomes angular dependent in the autoacceleration

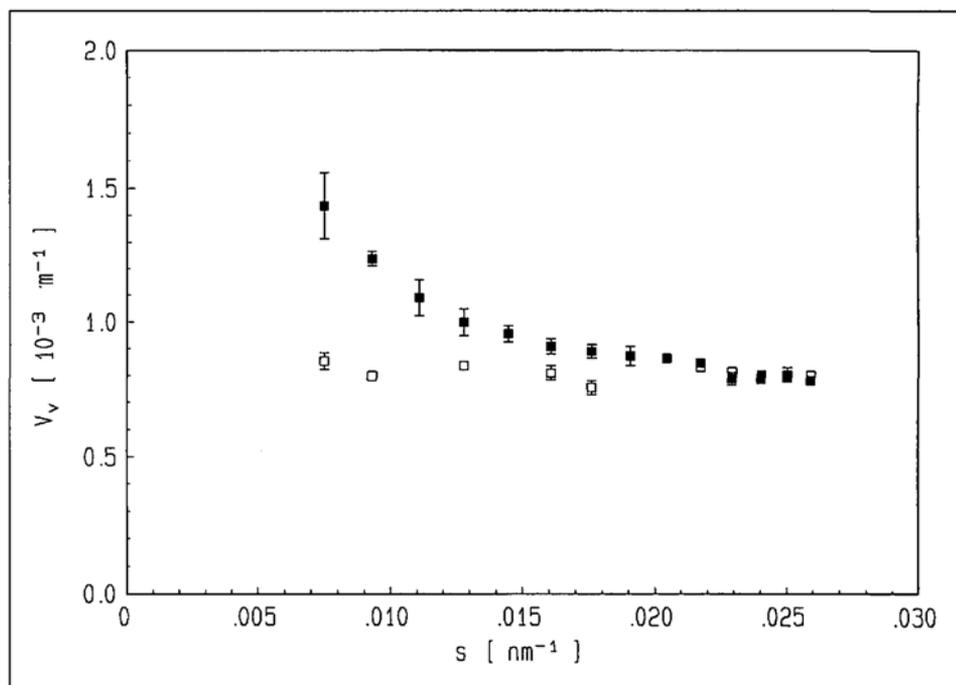


Fig. 5. V_V Component of light-scattering vs. magnitude of the scattering vector for methyl methacrylate after t = 708 min (□) and t = 715 min (■) polymerization at T = 90°

Table. Origin of Scattering Losses in Poly(methyl methacrylate) ($\lambda_0 = 633$ nm)

Origin of light scattering	Loss [dB/km]
Anisotropy fluctuations	3.7
Long-range and short-range density fluctuations in unannealed samples (Fig. 2)	41.7
Short-range density fluctuations in samples annealed 24 h at 180°	11.6
Short-range density fluctuations described by fluctuation theory Eqn. 19	12.9

range when T_g of the PMMA/MMA solution rapidly approaches the polymerization temperature T_s [7]. The angular dependence of V_V is also observed at lower conversions provided the solutions are cooled down to temperatures T close to T_g ($T \approx T_g + 20^\circ$).

Fig. 2 demonstrates that the V_V^D component of PMMA annealed far above T_g becomes independent of the scattering angle. In the absence of long-range density fluctuations, the V_V^D component may be calculated from Eqn. 12 using fluctuation theory. In the case of density fluctuations which extend over regions small compared to the wavelength of light, Eqn. 12 may be written in the form

$$V_V^D = \frac{4\pi^2}{\lambda_0^4} n^2 \langle \Delta n^2 \rangle V \quad (15)$$

where the correlation volume

$$V = 4\pi \int_0^\infty F(r) r^2 dr \quad (16)$$

is independent of s . Δn of glassy homopolymers is given by

$$\Delta n = \left(\frac{\partial n}{\partial \rho} \right)_T \Delta \rho + \left(\frac{\partial n}{\partial T} \right)_\rho \Delta T \quad (17)$$

where the second term may be neglected. With [3][11]

$$\langle \Delta \rho^2 \rangle = kT \kappa(T_g) \frac{\rho^2}{V} \quad (18)$$

Eqn. 15 yields

$$V_V^D = \frac{4\pi^2}{\lambda} n^2 \left(\rho \frac{\partial n}{\partial \rho} \right)^2 \kappa(T_g) \quad (19)$$

The values of V_V^D , and hence of α^D , calculated from Eqn. 19 are in close agreement with data measured for PS [3] and PMMA [6][7] in the absence of long-range density fluctuations (see also the Table).

3.2. Polymer Mixtures and Copolymers

It is assumed that the polymer mixtures and copolymers discussed in this section consist of two species with different refractive indices. In that case, concentration fluctuations c produce fluctuations of the refractive index

$$\Delta n = \left(\frac{\partial n}{\partial c} \right)_{T,\rho} \Delta c \quad (20)$$

which must be added to those described by Eqn. 17. Provided the concentration fluctuations extend over regions small compared to the wavelength of light, Eqn. 15 and 20 yield for the additional scattering

$$V_V^C = \frac{4\pi^2}{\lambda_0^4} n^2 \left(\frac{\partial n}{\partial c} \right)_{T,\rho} \langle \Delta c^2 \rangle V \quad (21)$$

$\langle \Delta c^2 \rangle$ is given by

$$\langle \Delta c^2 \rangle = \frac{cRT}{N_A V} \frac{1}{\frac{\partial \pi}{\partial c}} \quad (22)$$

where π is the osmotic pressure. Benoit *et al.* [12][13] have calculated $\delta\pi/\delta c$ for polymer mixtures and copolymers on the basis of the lattice theory. With the simplifying assumption that the volume occupied by each monomer unit is identical to that of the lattice cell ($V_A = V_B = V_0$), Eqns. 21 and 22 give for polymer mixtures [12–14]

$$\frac{K}{V_V^C} = \frac{1}{z_A(1-\phi)} + \frac{1}{z_B\phi} - 2\chi \quad (23)$$

$K = \text{constant}$

$z_A, z_B = \text{degree of polymerization of components A and B}$

$\Phi = \text{volume fraction of component B}$

$\chi = \text{Flory-Huggins interaction parameter}$

Since light-scattering data are not available Eqn. 3 may be used to estimate the scattering loss α^C of a miscible polymer blend. The results shown in Fig. 6 demonstrate that α^C is acceptable (≤ 100 dB/km) provided the difference in refractive indices of the two components is small and χ is negative. However, α^C strongly increases when χ becomes positive. In fact, V_V^D goes to infinity when χ equals one half of the first two terms in Eqn. 23. This condition reflects the phase separation of the system.

It is interesting to estimate the scattering loss of a system that is completely separated into two phases. With

$$\langle \Delta n^2 \rangle = \phi(1-\phi) \Delta n^2 \quad (24)$$

and with the assumption that the correlation volume is spherical, Eqn. 15 yields

$$V_V^C = \frac{2\pi^3}{3\lambda_0^4} n^2 \phi(1-\phi) \Delta n^2 D^3$$

where D ($D \ll \lambda$) is the diameter of the correlation volume. The results shown in Fig. 7 provide valuable information on the range of Δn and D where the scattering loss of a phase separated polymer blend is acceptable.

Concentration fluctuations in copolymers result from fluctuations in the chemical composition of the molecules. For copolymers, Eqn. 23 must be written in the form

$$\frac{K}{V_V^C} = \frac{1}{z \langle \Delta u^2 \rangle} - 2\chi \quad (26)$$

where $\langle \Delta u^2 \rangle$ describes the mean square fluctuation in chemical composition.

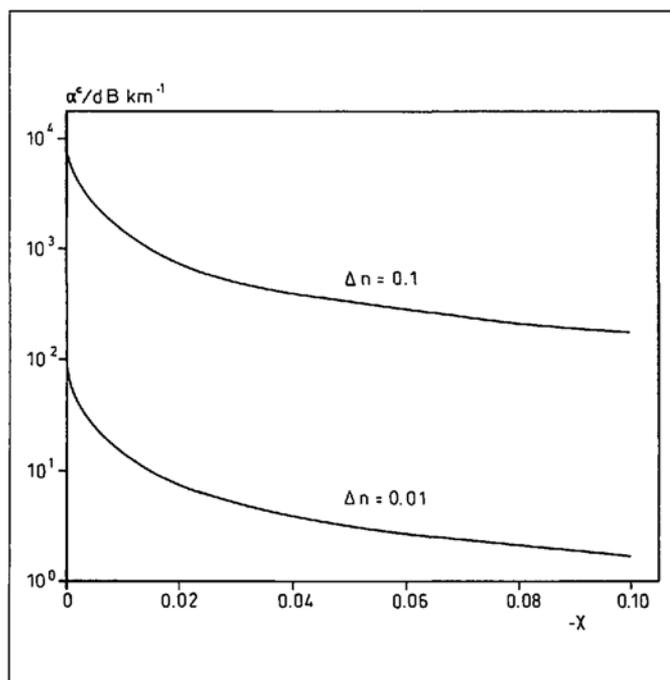


Fig. 6. Scattering loss by concentration fluctuations in a miscible polymer blend calculated from Eqn. 23 ($\lambda_0 = 633$ nm, $n = 1.5$, $V_0 = 1.66 \cdot 10^{-28}$ m³, $z_A = z_B = 1000$, $\Phi = 0.5$)

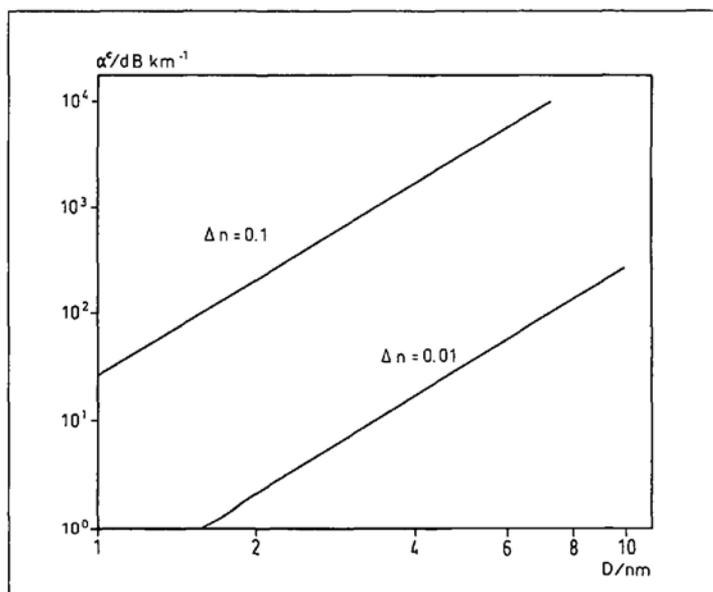


Fig. 7. Scattering loss of a phase separated polymer mixture with spherical correlation volume of diameter D ($\lambda_0 = 633$ nm, $n = 1.5$).

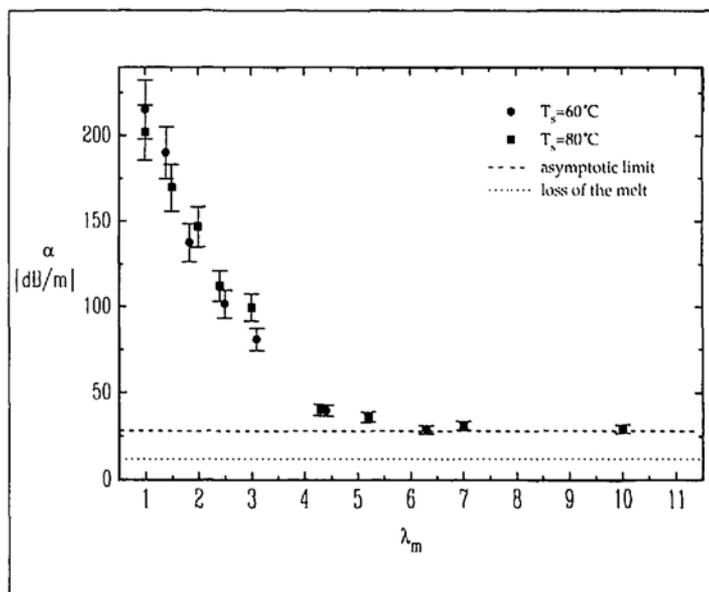


Fig. 8. Optical loss of poly(vinylidene difluoride-co-tetrafluoroethylene-co-hexafluoro-propylene) as a function of extension ratio at different drawing temperatures

$$\begin{aligned} \langle \Delta u^2 \rangle &= \langle u^2 \rangle - \langle u \rangle^2 \\ \langle u^2 \rangle &= \sum n_i u_i^2 / \sum n_i \\ \langle u \rangle &= \sum n_i u_i / \sum n_i \end{aligned} \quad (27)$$

n_i is the number of molecules with fractions u_i and $1 - u_i$ of A and B units, respectively. Light-scattering studies on statistical copolymers of fluoroacrylic acid-hexafluoroisopropylester and fluoroacrylic acid-trifluoroethylester [7] have shown that the contribution of α^2 to the total loss may be kept small while improving other physical properties such as the absorption loss.

4. Semicrystalline Polymers

Melt-crystallized polymers frequently exhibit a spherulitic superstructure which is the main origin of their high scattering losses. The question arises whether transformation of this structure into a fibre morphology is an effective method to reduce the scattering losses. In fact, Norris and Stein [15] have demonstrated that the deformation of polyethylene reduces the scattering intensities. To answer the question in more detail, experiments have been conducted on a statistical terpolymer consisting of vinylidene difluoride, tetrafluoroethylene and hexafluoro-propylene [16] [17]. This polymer has been used as cladding material in polymer optical fibres. Small-angle light-scattering and small-angle X-ray scattering have shown that deformation of the melt-crystallized terpolymer transforms the spherulitic into a fibre morphology. The optical loss measured by the transmission of light in fibre direction decreases with increasing draw ratio λ_m and finally reaches a plateau as shown in Fig. 8. The plateau value is only

two times higher than the loss of the melt which exceeds that of PMMA because of impurities. Small-angle and wide-angle light-scattering experiments are in progress to study the effect of the fibre morphology on the scattering loss in more detail. The preliminary results presented in Fig. 8 indicate that deformation may be a promising method to reduce the scattering loss of semicrystalline polymers.

5. Conclusions

In the absence of impurities and defects the scattering losses of polymer optical fibres are caused by anisotropy, density and concentration fluctuations in the fibre materials. Light-scattering of glassy homopolymers results from anisotropy and density fluctuations. It has been shown for poly(methyl methacrylate) that long-range density fluctuations may be produced in the autoacceleration range of polymerization when T_g of the polymer/monomer solution rapidly approaches the polymerization temperature. These fluctuations are reduced by annealing the material at temperatures far above T_g . The remaining scattering loss is close to the theoretical value calculated from fluctuation theory. Glassy polymer mixtures and copolymers exhibit additional scattering from concentration fluctuations. This contribution has been estimated theoretically. The results have shown that under appropriate conditions both polymer mixtures and copolymers are potential candidates for polymer optical fibre materials. Melt-crystallized polymers frequently exhibit a spherulitic superstructure which is the main origin of their high scattering losses. Studies on a terpolymer consisting of vinylidene difluoride, tetrafluoroethylene and hexafluoro-

propylene have demonstrated that transformation of the spherulitic into a fibre morphology is a promising method to reduce the scattering losses drastically.

This work was supported by the Bundesministerium für Forschung und Technologie. The author gratefully acknowledges funds from the Fonds der Chemischen Industrie. The studies on semicrystalline polymers greatly benefitted from the fruitful collaboration with Dr. Dittmer (Hoechst AG).

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