

Characterization of Multiplets in a Nd³⁺-Doped Polymer Optical Fiber with Low Ion Concentration

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ABSTRACT: A new model is established to infer a ratio of multiplet ions to the total ions (ρ) based on rate equations of ionic transferring between excited and unexcited states, which is designed for rare earth containing polymer optical fiber (POF) with low ion concentration ranging from 30 to 200 ppm. A step-index (SI) Nd³⁺-doped POF was made from a preform which was prepared by using bulk polymerization of methyl methacrylate (MMA) with a certain amount of neodymium octanoate (NOA) as a dopant, 2,2-

azoisobutyronitrile (AIBN) as an initiator, and *n*-butyl mercaptan as a chain-transfer agent. The measurement of transmission at 810 nm of the Nd³⁺-doped POF was made by fitting experimental data and by using the theoretical model, the values of ρ at different Nd³⁺ concentration could be obtained. The result showed that the ratio is 0.03, 0.08, and 0.3 for Nd³⁺-doped POF at Nd³⁺ concentrations of 70, 100, and 200 ppm, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2033–2040, 2002

INTRODUCTION

Much interest has been devoted to rare earth doped polymer optical fiber (POF) in the past years^{1–3} because of its unique light amplification property. The POF is usually obtained from a preform made of rare earth doped polymers, which are prepared by polymerization of the mixture of monomers and rare earth ion containing molecules, such as chelates² or organic salts.³ The structural morphology of this rare earth doped polymer is a key point determining its properties, especially the ion aggregation, or the multiplet, structure formed within rare earth doped polymers. From the point of morphology, the ion aggregation is of a similar structure as one in random ionomers, although there is a difference in the preparation processes of the two polymers.

A number of models for the morphology of random ionomers were proposed to explain already existing experimental observations concerning the ionomers. In these studies, all the models are based on the materials with ion concentrations ranging from 1.0⁴ to 18 mol %.⁵ In 1990, Eisenberg et al.⁶ proposed a new model of clustering in random

ionomers, which was originated from the multiplet-cluster model proposed in 1970. This model accounts for wide ranges of experimentally observed phenomena. The clusters behave as if they were phase-separated from the regions of more mobile segmental motion in that they exhibit their own glass transition temperature (T_g), which is significantly higher than the T_g of the unclustered component. In these regions also, one would expect a most prevalent intermultiplet spacing. This spacing accounts for the characteristic ionic peak in the small-angle X-ray scattering (SAXS) profiles of these materials above a certain ion content.

The ionomers studied in such experiments have relatively high ion concentration that is generally beyond 1 mol %.⁶ The ionomers within 1000 ppm ion concentration have rarely been studied before. One of the reasons is that there are no available experimental phenomena to demonstrate the existence of multiplet in the bulk with extremely low ion concentration. In this work, one Nd³⁺-doped POF was made with very low ion concentration. The transmission of the fiber is affected by rare earth ions doped inside of the material because the optical path length of the fiber is long enough and rare earth ions have many energy levels to interact with transmitting light, although the POF has only very low ion content. Based on rate equations of ionic transferring between excited and unexcited states, the following model is set up to study the structure of ion aggregations possibly existing in the Nd³⁺-doped POF with extremely low concentration < 500 ppm.

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EXPERIMENTAL

Neodymium octanoate (NOA) was made from neodymium oxide. The oxide was dissolved in concentrated nitric acid by heat to form a solution of neodymium nitrite. Adding it to the solution of sodium carbonate with a concentration of 10%, solid Nd^{3+} carbonate was obtained with nearly 100% product. Being desiccated in a vacuum oven at 80°C for 2 h, the solid Nd^{3+} carbonate was titrated with excess octanoic acid by a constant temperature of 80°C. Then, the reacted solution was filtrated and the filtrated solution was put into a large amount of acetone. A great deal of sedimentation was obtained, which is NOA according to IR and elementary analysis.

The step-index (SI) Nd^{3+} -doped POFs were fabricated as follows. Purified MMA, 0.01 mol/l 2,2-azoisobutyronitrile (AIBN) as an initiator, 0.03 mol/l *n*-butyl mercaptan as a chain-transfer agent, and a specified amount of NOA were mixed in a vessel and heated at 90°C for prepolymerization and then heated at 50°C for 12 h to polymerize the monomer. After the polymerization, the temperature was gradually increased to 80°C and kept for 12 h to complete the polymerization. Then, a preform rod with a diameter of 10 mm was prepared. Compared with pure poly(methyl methacrylate) (PMMA), it had a higher T_g (=109.5°C for Nd^{3+} -doped PMMA, about 10°C higher than that of pure PMMA at the same condition).³ When the temperature was between 180 and 200°C, the preform was drawn into an unclad optical fiber. At different drawing velocity and temperature, fibers with different diameters were obtained. The fibers were clad with silica, the refractive index of which was 1.4105. The numerical aperture of the Nd^{3+} -doped POF was 0.49 with a core refractive index of 1.4931. Rare earth ions have poor solubility in an organic matrix, whereas they are compatible with inorganic matrix. With the use of a developed method used before,³ NOA was found dissolved into PMMA when NOA concentration is within several hundred parts per million.

Fiber transmission measurements are made for three Nd^{3+} -doped POFs by using a diode-laser array at 810 nm as a source. The output power was measured by an AV2491 powermeter. The three Nd^{3+} -doped POFs had a same length of 30 cm with different concentrations of 70, 100, and 200 ppm. The radius of these fibers is 100 μm and they are multimode fibers. In the numerical calculation, we used these experimental parameters⁷: $\sigma_p = 2 \times 10^{-24} \text{ m}^2$, $h\nu_p = 2.47 \times 10^{-19} \text{ J}$, $A_{\text{eff}} = 2 \times 10^{-8} \text{ m}^2$, $\tau_{\text{rad}} = 10^{-5} \text{ s}$, and $\tau_c = 10^{-7} \text{ s}$.

RESULTS AND DISCUSSION

Theoretical model based on rate equations

It is well known that ionomers are typically defined as polymers with acidic side group neutralized by cations⁸ and that these side groups join with the main

chain through covalent bonding. In this article, Nd^{3+} -doped polymer optical fiber (Nd^{3+} -doped POF) is selected as an experimental sample to set up a new model concerning metal-containing polymer with low concentrations. The fiber is made from a preform in which a preparation of NOA is blended into methyl methacrylate (MMA) first, and then the mixture was polymerized by free-radical polymerization. Within the preform, NOA links with the PMMA chain through a coordination field of Nd^{3+} ion. The principal multiplet properties around metal ions should be similar to each other in both kinds of ionomers.

The optical properties of most trivalent lanthanide complexes in the near-ultraviolet, visible, and near-infrared spectral regions can be accounted for in terms of intraconfigurational $4f-4f$ radiative transitions.^{9,10} Along with these radiative transitions, energy transference is followed. Cross relaxation takes place between close ions as occur in multiplets. For Nd^{3+} , this energy transference occurs between an excited ion and a ground ion. The ion in excited state ${}^4\text{F}_{3/2}$ (donor) gives half-energy to the acceptor in ground state ${}^4\text{I}_{9/2}$, so that both ions end up in the intermediate state ${}^4\text{I}_{15/2}$, from which they both relax nonradiatively to the ground state (see Fig. 1).

In this model, Nd^{3+} -doped POF is used as a sample in which length dimension is in the direction of light transmission (*z*-axis). Because of the low rare earth ion concentration in Nd^{3+} -doped POF, we assumed that (1) a multiplet contains two Nd^{3+} ions, which is expressed as a Nd^{3+} pair in this article; (2) there is no interaction between ions of different multiplets. In this case, the rate equations for Nd^{3+} ions in the fiber to transfer between excited and unexcited (ground) energy states can be written as follows¹¹:

$$\frac{dN_1^p}{dt} = -\frac{N_1^p}{\tau} - \frac{N_1^p}{\tau_{\text{rad}}} + 2\frac{N_2^p}{\tau_{\text{rad}}} + 2\omega_p N_0^p - \omega_p N_1^p \quad (1)$$

$$\frac{dN_2^p}{dt} = -2\frac{N_2^p}{\tau_{\text{rad}}} + \omega_p N_1^p \quad (2)$$

$$\frac{dN_e^s}{dt} = -\frac{N_e^s}{\tau_{\text{rad}}} + \omega_p N_g^s \quad (3)$$

In the equations shown above, N_0^p , N_1^p , and N_2^p are concentrations of the unexcited Nd^{3+} pair, single-excited Nd^{3+} pair, and doubly excited Nd^{3+} pair, respectively. N_g^s and N_e^s are concentrations of unpaired Nd^{3+} in the ground state and excited state, respectively. τ_c is the time constant of cross relaxation and τ_{rad} is the lifetime of the metal state. ω_p is the pump rate and is of following form:

$$\omega_p = \frac{p\sigma_p}{h\nu_p A_{\text{eff}}} \quad (4)$$

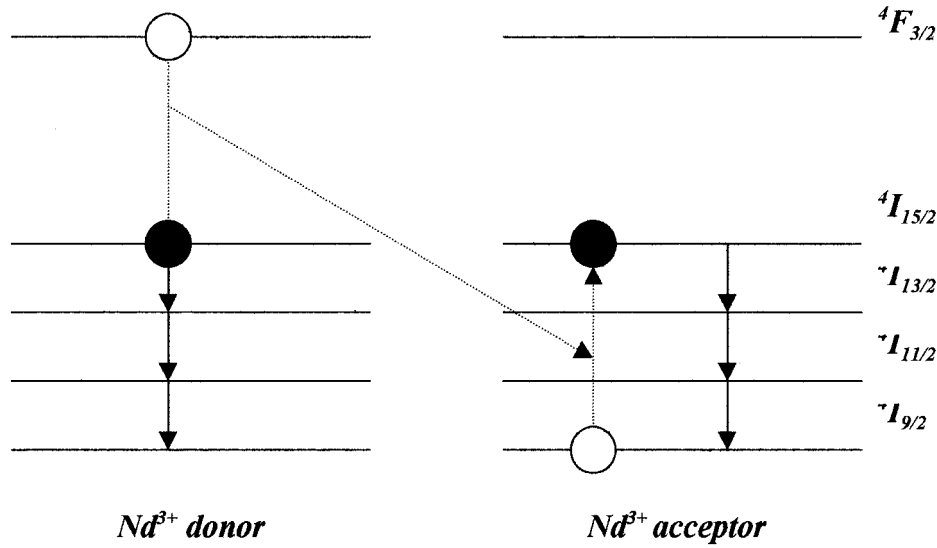


Figure 1 Cross relaxation process for Nd³⁺ ions within one multiplet. Open circle: initial position of the electrons; closed circle: final position; dashed lines: energy transfers; solid lines: nonradiative transitions.

in which, p is the pump power, σ_p is the absorption cross section, h is plank constant, ν_p is pump frequency, and A_{eff} is the effective mode square of pump light. Because each pair has two ions, the total excited ion concentration, the unexcited ion concentration, and the total ion concentration are listed as the following:

$$N_e = 2N_2^p + N_1^p + N_e^s \quad (5)$$

$$N_g = 2N_0^p + N_1^p + N_g^s \quad (6)$$

$$N_{\text{tot}} = N_e + N_g \quad (7)$$

The ratio of multipletted ions to the total ions is defined as ρ ; then, the steady solution of eqs. (1)-(3) can be worked out as follows:

$$N_g = \frac{N_{\text{tot}}\omega_{\text{rad}}}{\omega_p + \omega_{\text{rad}}}(1 - \rho) + \rho N_{\text{tot}} \frac{\omega_c + \omega_p + \omega_r}{(\omega_c + 2\omega_p + \omega_p^2/\omega_{\text{rad}} + \omega_{\text{rad}})} \quad (8)$$

In eq. (8), the last item was imputed to energy transfer between multipletted ions where ω_{rad} is the transition rate from metastable state and ω_c is the cross relaxation rate, that is,

$$\omega_{\text{rad}} = \frac{1}{\tau_{\text{rad}}} \quad \omega_c = \frac{1}{\tau_c} \quad (9)$$

When a stimulating energy power (p), pump power, launched into Nd³⁺-doped POF and after steady state was established, the pump power will change along the z direction in following form:

$$\frac{dp}{dz} = -\sigma_p N_g p \quad (10)$$

In eq. (10), amplified stimulated emission and the background absorption of POF was ignored because the infrared fluorescence caused by stimulated emission is strongly absorbed by the host of Nd³⁺-doped POF and considerably short lengths of POF used as samples in the experiments.

Equation (10) was integrated numerically along the fiber length (z axis) to obtain the fiber transmission $T_f = p(\lambda)/p(0)$, where $p(0)$ was the launched pump power and $p(\lambda)$ was the output pump power at the fiber length of λ . It is obvious that the transmission was closely related to the basic multiplet parameter, ρ , as other parameters are fixed under experimental conditions. So, with the fiber transmission data, ρ can be numerated through eq. (10).

Multiplets in a Nd³⁺-doped polymer optical fiber

As stated in Eisenberg's model proposed in 1990, the formation of multiplets is affected by the strength of the electrostatic interactions between the ions, the elastic forces of the chains, the ion content of ionomer, and the dielectric constant of polymer. Different structure of ionic salt and different main chain of polymer will result in the difference of the correlative experimental phenomena. Before studying the structure of the multiplets containing two ions in polymeric bulk, the solid structure of NOA was discussed.

Infrared spectrum of NOA showed that there are two strong absorption peaks located at 1541.7 and 1454.7 cm⁻¹, respectively. They are absorptions of antisymmetrical (ν_1) and symmetrical (ν_2) vibrations of

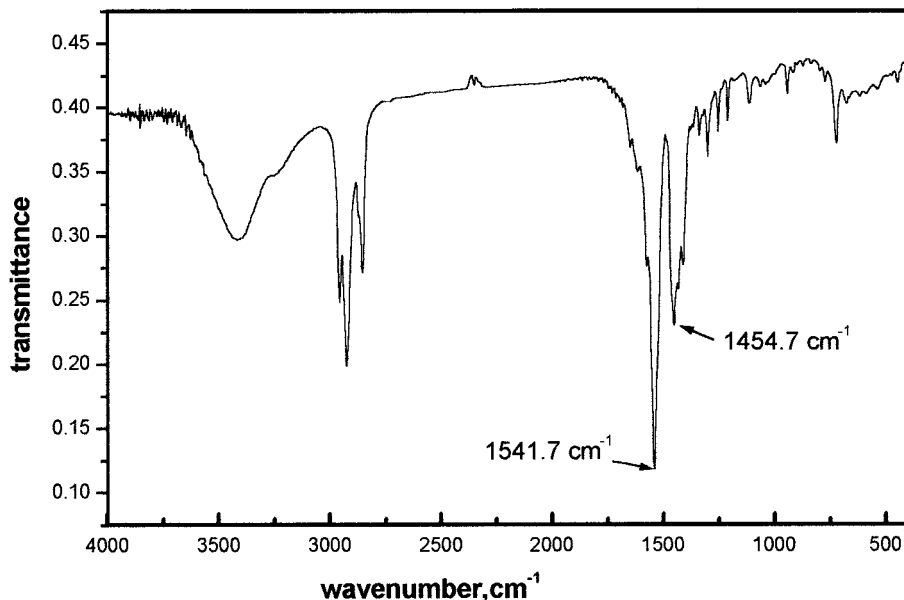


Figure 2 Infrared spectrum of neodymium octanoate (NOA). The numbers labeled in the figure refer to the wavenumbers of antisymmetrical and symmetrical vibration absorption of carboxyl group, respectively.

the carboxyl group accordingly. The frequency difference ($\Delta\nu$) between these two peaks is 87 cm^{-1} . The spectroscopic studies on the structure of carboxylate complexes were carried on broadly.^{12–15} It was found that a relationship between the o-c-o angle and the frequency difference ($\Delta\nu = \nu_1 - \nu_2$) exists. Generally speaking, there are two kinds of structures of Nd^{3+} octanoate, one is a chelating structure and the other is a bridging structure. It is known that in chelating acetates the o-c-o angle will be smaller than in bridging acetate,¹⁶ which is confirmed by the structural evidence: chelating acetate angles^{17,18} being 111° and 121° , bridging angles^{19–21} being 125° , 123° , and 124° . Grigor'ev¹⁶ calculated the effect of changing the o-c-o angle without changing the force constant. He found that increasing this angle should increase ν_1 and decrease ν_2 , and hence, increase $\Delta\nu$. The classical frequency difference of the coordinate linkage between ion and carboxyl group is 140 and 80 cm^{-1} for bridge linkage and chelation linkage, respectively.²² It was reported that chelation linkage was formed when the frequency difference of two peaks is below 133 cm^{-1} .²³ Figure 2 is the IR spectrum of NOA and from which $\Delta\nu$ of 87 cm^{-1} can be obtained. This data shows NOA is of chelation linkage, as given by the two-dimension structure in Figure 3.

In this model, multiplets containing two Nd^{3+} ions are first assumed to exist in low ion concentration bulk. Our primary justification for the assumption is consistent with our experimental results to be given later. The dominant parameter that affects multiplet formation is the strength of the electrostatic interactions between NOA, which is determined by the sizes of the ions, and the partial covalent character of the ionic band. The characteristics of the host polymer are

also important in determining the extent of multiplet formation in a random ionomer. Low dielectric constant and low T_g of the host polymer tend to favor ionic aggregations. In NOA-PMMA bulk, each multiplet containing two Nd^{3+} ions effectively anchors the polymer chain indirectly through coordination interaction. Because the NOA is unreactive to polymerization, the fundamental structure of NOA is thought as unchanged after it was doped into the PMMA bulk by the method described above, although Nd^{3+} ions link with the main chain of PMMA by coordination bonds. The structure of the aggregate containing two Nd^{3+} ions is shown in Figure 4. It is well known that ion pairs anchor on the polymer main chain by covalent bond in classical ionomers. In NOA-PMMA, ion pairs anchor on the main chain by coordination bonds between Nd^{3+} ions and the main chain. When a multiplet containing two Nd^{3+} ions formed, the action of multiplets on the main chain in NOA-PMMA is rela-

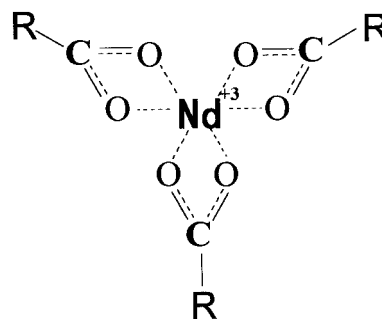


Figure 3 Two-dimensional schematic structure of NOA chelation linkage, in which each ester group bonded the same neodymium ion by two coordinate bonds between oxygen and neodymium ions and $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

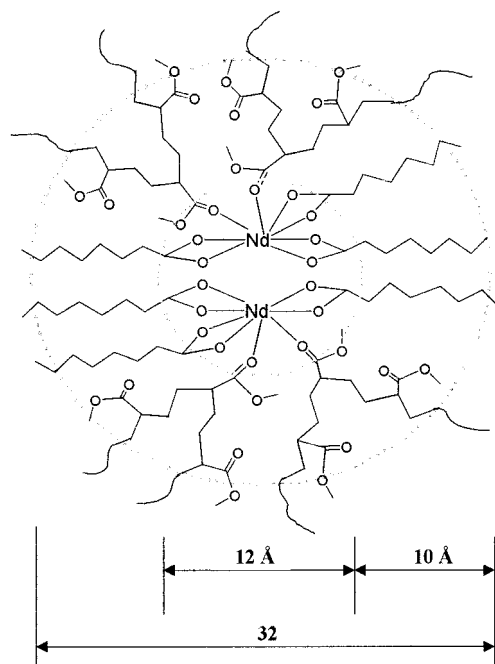


Figure 4 Two-dimensional schematic diagram of a multiplet containing two Nd^{3+} ions, the core diameter of which is 12 Å that is based on calculations of bond length and atom size.

tively weaker than that in classical ionomers because of the bond difference between ion pair and main chain. Hence, the mobility of the polymer chain in the immediate vicinity of a multiplet is expected to be less greatly restricted than classical ionomers. Thereby, the interaction between these multiplets is relatively stronger, which could result in more easily gathering of multiplets to form clusters. Along with the increasing ion concentration, the number of Nd^{3+} ions within a multiplet will also augment according to the increasing density and interaction of ions, which also can accelerate the progression of multiplets gathering. The phase-separated phenomena in NOA-PMMA bulk is observed when ion concentration is $>0.2\%$, which is greatly less than the reported phase-separated concentration in the previous model.^{24-26,6}

Assuming that Nd^{3+} ions are distributed evenly in the PMMA bulk, the distance between adjacent isolated ions can be calculated separately by neglecting the size of NOA. Supposing that the Nd^{3+} ions are all singly distributed in polymer bulk, the distance is 167 Å for the ion concentration of 30 ppm, 112 Å for ion concentration of 100 ppm, and 88.6 Å for ion concentration of 200 ppm. It can be deduced that the distance will be greater when multiplets formed, which is caused by the decrease of the number of isolated ions. A series of schematic diagrams of the distribution of isolated Nd^{3+} ions and the multiplets containing two Nd^{3+} ions in polymeric bulk are shown in Figures 5-6. A distance ranging from 20 to 80 Å between multiplets within a cluster was reported,²⁷ which is much less

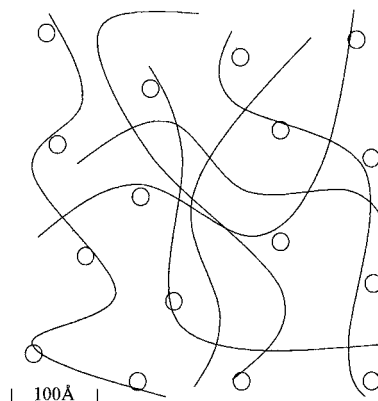


Figure 5 Schematic diagram representing the solid structure of NOA-PMMA with Nd^{3+} ion concentration of 30 ppm assuming no multiplets formed. Open circle represents a single NOA molecule.

than the data between adjacent multiplets shown in Figure 6. The core diameter of the multiplet can be estimated as 12 Å, which was based on the calculation of bond length and atom size. The dimension of the region of restricted mobility can be estimated as 10 Å.⁶ Thereby, the radius of multiplet of two Nd^{3+} ions can be estimated as 16 Å by adding the core size and the size of region of restricted mobility together, which was shown in Figure 6. A cluster cannot be formed unless the distance between multiplets is no more than the diameter of a multiplet. By comparing these distances between adjacent Nd^{3+} ions with the diameter of a multiplet containing two Nd^{3+} ions, it is very clear that clusters did not form in such ion concentrations. From this deduction, it can be seen that assumptions given in the theoretical model are reasonable.

For a POF sample with several hundred ppm of Nd^{3+} ion concentration, it is also reasonable that the

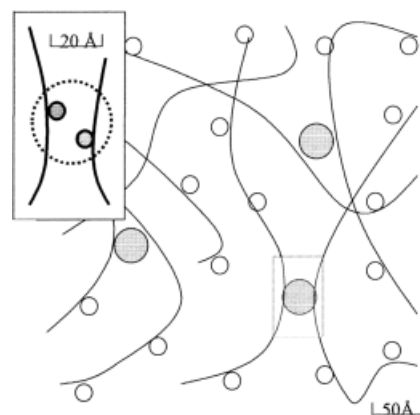


Figure 6 Schematic diagram of NOA-PMMA with the multiplets containing two Nd^{3+} ions formed when the Nd^{3+} ion concentration is 200 ppm. The inset diagram is the amplified schematic diagram of a multiplet containing two Nd^{3+} ions. Open circle represents a single NOA molecule and solid circle represents a multiplet composed of two NOA molecules.

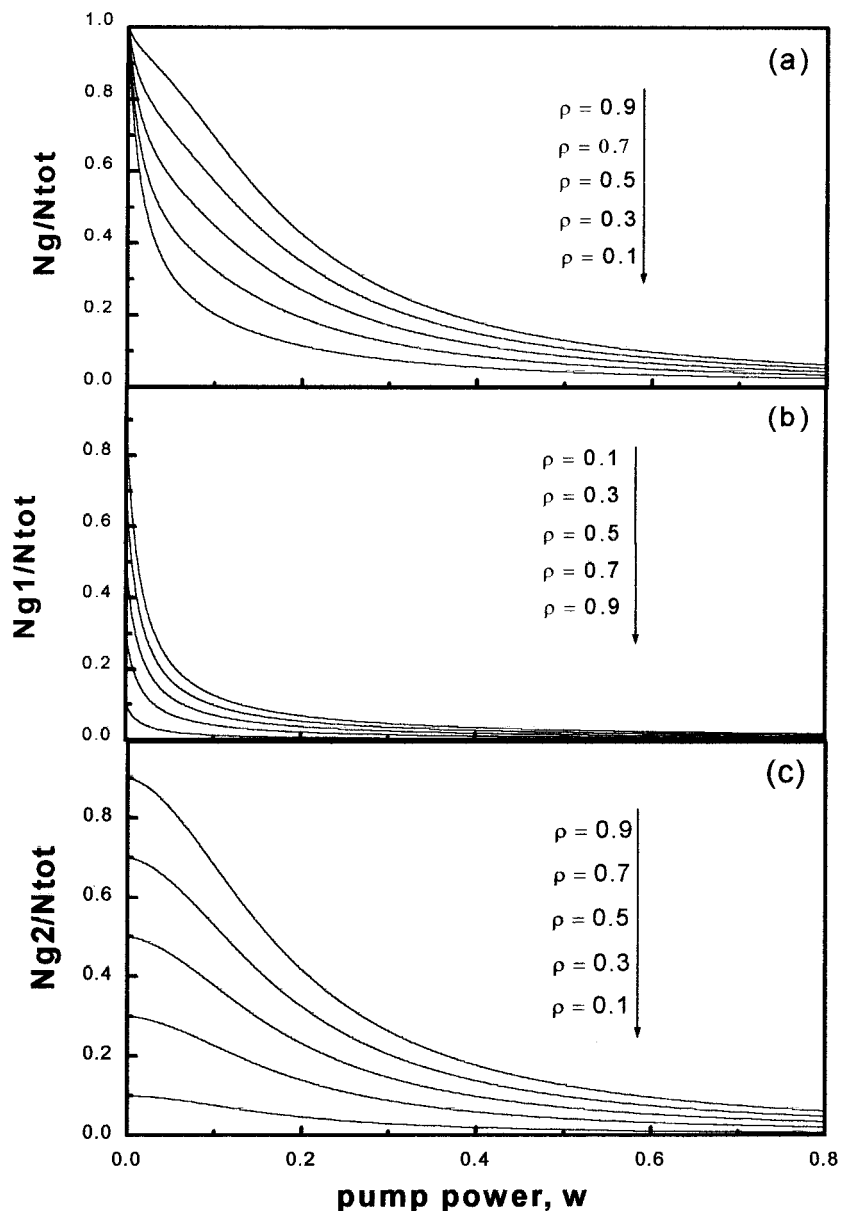


Figure 7 Relation curves between items of eq. (8) and pump power. (a) Relationship between combined unexcited concentration and pump power; (b) the relationship between unexcited concentration of isolated Nd^{3+} ions and pump power; (c) the relationship between unexcited concentration of multipletted Nd^{3+} ions and pump power. The number in each figure refers to the value of ρ .

POF sample made from bulk samples has the same morphology with the bulk sample. When a light is introduced into the fiber, and a steady state is established, various rate processes described by eqs. (1)-(3) will reach a equilibrium. Under this circumstance, N_g , the unexcited ion concentration of Nd^{3+} in the ground state, can be calculated according to eq. (8), and affected by N_{tot} , ρ , and light power, P . N_g in eq. (8) can be divided into two parts. The first item is contributed to the isolated Nd^{3+} ions (N_{g1}) and the second item to multipletted Nd^{3+} ions (N_{g2}). Figure 7 shows each item changes as P and ρ increase. From Figure 7, it can be figured out that all of N_g , N_{g1} , and N_{g2} decrease dramatically with pump power increasing. In Figure 7(a),

values of N_g for each ρ value remain unchanged at about 0.05 of N_g/N_{tot} when pump power P approaches 0.8 W. This mainly resulted from the item of N_{g2} . If there were no multiplets existing in the sample, N_g , which only comprises N_{g1} , would disappear when P is large enough, as shown in Figure 7(b) given by this model. N_{g1} contributes most to N_g when the value of ρ is small. When the value of ρ increases, N_{g1} decreases, but both N_g and N_{g2} increase. It can be explained by the fact that excited Nd^{3+} ions in multiplets can reach ground state more easily and more rapidly because the cross relaxation between Nd^{3+} ions would take place in a short time as $\tau_c = 10^{-7}$ s for a couple of Nd^{3+} ions within one multiplet. When

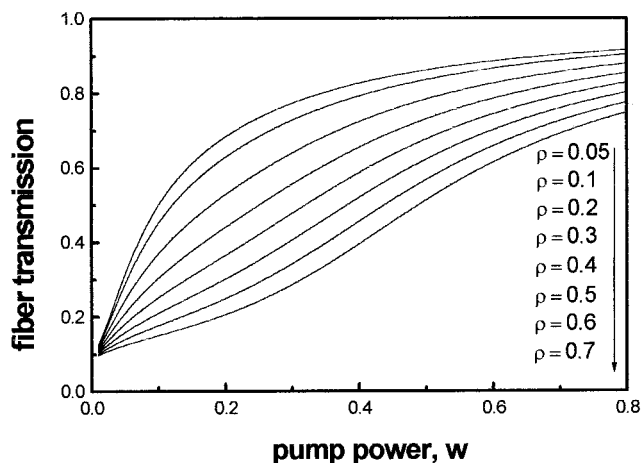


Figure 8 Theoretical curve of relationship between fiber transmission and pump power with different values of ρ in NOA-PMMA bulk of 200 ppm Nd^{3+} ion concentration. The number labels in this figure mean the values of ρ . In calculating, the following parameters were used: $\sigma_p = 8 \times 10^{-24} \text{ m}^2$, $h\nu_p = 2.47 \times 10^{-19} \text{ J}$, $A_{\text{eff}} = 1.2 \times 10^{-11} \text{ m}^2$, $\tau_{\text{rad}} = 8 \times 10^{-4} \text{ s}$, and $\tau_c = 10^{-7} \text{ s}$.

multiple concentration, ρ , increases, Nd^{3+} ions in the ground state, N_g , would also increase.

Assuming a POF sample with 200 ppm of Nd^{3+} ion concentration, given different ρ values, theoretical curves of relationship between transmittance and pump power resulted from eq. (10) are shown in Figure 8. The curves are of similar shape, but have different transmittance at the same pump power. A small difference can be found in the curve shape between curves with $\rho > 0.5$ and $\rho < 0.5$. For curves with $\rho > 0.5$, higher rates of transmittance over pump power can be observed when the power is larger than 0.3 W. This may be explained in terms of the existence of more multiplets and cross relaxation in the system. Another reason will come from the limitation of this theoretical model. During integration of eq. (10), one important assumption is that there are only multiplets composed of two Nd^{3+} ions in the samples. This is true when the concentration of Nd^{3+} ions is low, but when the concentration increases, that is, ρ increases, multiplets composed of more Nd^{3+} ions, or cluster, may form in the sample. Under this circumstance, more complex models containing more rate processes or other models dealing with high ion content ionomers will be considered. For the $\rho < 0.5$ system, it is interesting to note that each curve can be made for its own ρ value, which means that each Nd^{3+} -doped POF sample has its own characteristic transmittance curve, although it has very low ion concentration. Therefore, from this model deduced above, it can be expected that POF samples with different Nd^{3+} ion concentration will have different curves, as shown in Figure 8.

Under different pump power, fiber transmissions of SI-type POFs doped with 70, 100, and 200 ppm of Nd^{3+} ion concentrations were measured and the re-

sults shown in Figure 9, in which experimental data points are symbolized as \square , \triangle , and \circ for the POF with Nd^{3+} ion concentrations of 200, 100, and 70 ppm, respectively. It can be observed in Figure 9 that for each Nd^{3+} concentration the fiber transmissions increase as the pump power increased. At high pump power of nearly 500 mW, the fiber transmissions reach a constant value and a residual absorption could not saturate. For different Nd^{3+} ion concentrations, the value of the residual absorption is different. This can be attributed to energy transference between two Nd^{3+} ions within a multiplet.

Adopting the theoretical model described above, three ρ values for Nd^{3+} -doped POF samples with 70, 100, and 200 ppm Nd^{3+} ion concentrations were estimated. The solid lines in Figure 9 are theoretical curves and obtained by selecting a fitting parameter ρ . The value of ρ was 0.05 for the fiber with a concentration of 70 ppm, 0.1 for the concentration of 100 ppm, and 0.3 for the concentration of 200 ppm, respectively. It is mentioned in Eisenberg's model proposed in 1990 that a multiplet may contain only two metal ions as well as a quartet when the ion concentration is low enough.¹⁸ However, what degree the ion concentration decreases to while the multiplet containing two Nd^{3+} ions is formed is dependent upon many factors. The result above provides quantitatively a description of the probability of the existence of multiplet containing two Nd^{3+} ions at certain low ion concentrations and critical Nd^{3+} ion concentration for forming the multiplet will be within 100 ppm.

It can be deduced from the data of ρ versus Nd^{3+} ion concentration shown above that the larger ion concentration, the bigger the value of ρ . From the results, we can also see that the fraction of multipletted

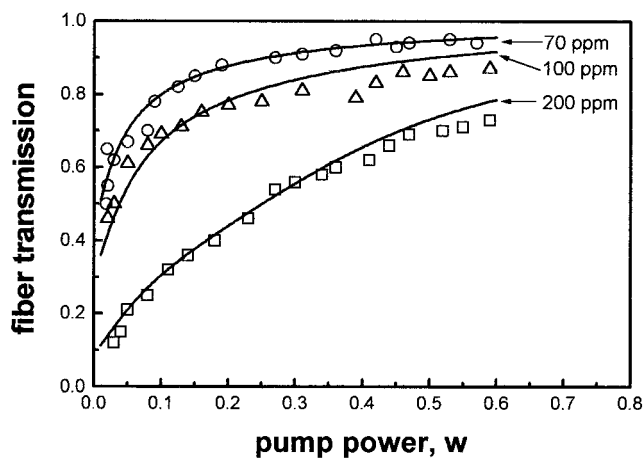


Figure 9 Transmission data of the three different fibers and best fits of the model with Nd-Nd pairs (solid lines). \circ , \triangle , and \square refer to experimental data points of three fibers: 70 ppm, 100 ppm, and 200 ppm, respectively. Theoretical simulation used following parameters: $\sigma_p = 8 \times 10^{-24} \text{ m}^2$, $h\nu_p = 2.47 \times 10^{-19} \text{ J}$, $A_{\text{eff}} = 1.2 \times 10^{-11} \text{ m}^2$, $\tau_{\text{rad}} = 8 \times 10^{-4} \text{ s}$, and $\tau_c = 10^{-7} \text{ s}$.

ions, ρ , is lower than 0.3 when the ion concentration is within 200 ppm. As we defined above, ρ , is the ratio of multipletted ions to the total ions and a multiplet is an aggregate containing two Nd^{3+} ions. Thereby, it can be inferred that a large part of the Nd^{3+} ions are distributed evenly in the polymer bulk when ion concentration is <200 ppm and only a small part of Nd^{3+} ions joined together to form a multiplet. Each multiplet links two or more PMMA chains together. These multiplets behave as a conventional crosslink. Therefore, the NOA-PMMA with such ion concentration can be viewed as a conventional ion crosslink polymer and these multiplets may influence the properties of the material in a similar fashion as well as ion crosslink polymers. In addition, as the multiplets formed in rare earth doped POF will affect the photonic properties, the result given above will be a guideline for designing active POF.

CONCLUSION

In summary, a new model based on the rate equation was set up to infer the multipletted Nd^{3+} ion ratio by the measurement of fiber transmissions. When the concentration was <200 ppm, the ratio of multipletted ion was < 0.3, which showed the formation of multiplets containing two Nd^{3+} ions as well as dominant existent form of the isolated Nd^{3+} ions in such ion concentrations. Then, the schematic diagram of the solid structure of NOA-PMMA with low Nd^{3+} ion concentration was described, and based on the solid structure, many properties can be predicted. This model provides a new method to explore the solid structure of rare earth ion containing polymer with low ion concentration.

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