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Conjugated polymer in isolated and aggregated chain environments studied by amplified spontaneous emission

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Aggregate formation of a conjugated polymer in solutions containing good and poor solvents is studied by amplified spontaneous emission (ASE). It is proved that ASE originates only from isolated polymer chains. For sufficient quantity of the poor solvent, aggregates are formed at the expense of the isolated chains, reducing substantially the optical gain. The critical polymer concentration for aggregation and the size distribution of the aggregates formed are determined by using a model based on thermodynamic principles. The number of isolated chains involved in aggregates of a specific size decreases as aggregates become larger incorporating up to seven chains.

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Conjugated polymers combining enhanced mechanical and optoelectronic properties have been applied as active media in photopumped laser systems[1–4] and organic light emitting devices (OLEDs).[5,6] For developing an efficient polymer LED or even an electrically pumped polymer laser, a comprehensive understanding of the optical properties of conjugated polymers and how these are influenced by polymer aggregates is imperative.[7–9] A favorable method for studying this influence is applied by using polymer solutions with good and poor solvents.[10–14] The addition of a poor solvent into a polymer solution causes chain aggregation which can be systematically controlled by changing the poor solvent quantity. The critical polymer concentration for aggregation as well as the number of polymer chains involved in aggregates are of major importance in this investigation. Research on aggregated polymer solutions has been mainly based to date on steady state and time-resolved fluorescence spectroscopy for studying the energy states variation[13,14] and the excited state dynamics[10–12] respectively. Recently, we directly studied stimulated emission (SE) through amplified spontaneous emission (ASE) in aggregated polymer solutions and concluded spectroscopically that ASE radiation originates only from the isolated chains.[15] This conclusion justifies the use of ASE for further research on polymer solutions giving a direct insight on the aggregates formation.

In this work, a quantitative affirmation of our previous spectroscopic results is attempted by measuring the SE cross sections through ASE in isolated and aggregated liquid chain environments. A comparison of these cross sections leads to the conclusion that the isolated chains existing in both environments are responsible for the ASE. Additionally, we present a detailed study of the aggregation procedure based on thermodynamic principles by analyzing ASE measurements of polymer solutions with different fractions of the poor/good solvent volume. Specifically, the isolated chains concentration, the critical polymer concentration for aggregation and the distribution of the number of polymer chains involved in aggregates are determined.

The polymer studied is a partially conjugated poly(phenylene vinylene) derivative containing alternating conjugated and nonconjugated segments, and it was recently synthesized[16] and characterized[15] as a laser medium in the blue spectral region. Its chemical structure is shown in the inset of Fig. 1 while its molecular weight is approximately 3600. The isolated chain environment was prepared by dissolving the polymer in tetrahydrofuran (THF) solvent (0.2 wt. %) while the aggregated ones were prepared by gradually adding a poor solvent (MeOH) into the initial polymer /THF solution. As pumping source a commercial N_2 pulsed laser with 337-nm wavelength, 5-ns pulse duration and 1-Hz repetition rate was used. Its beam was focused through a cylindrical lens on the sample forming an excitation stripe across it[17] with dimensions $0.45\times 20\ \mathrm{mm}^2$. The peak intensity of each pumping pulse was $0.92\ \mathrm{MW/cm}^2$, with a pulse to pulse fluctuation of ~3%. The intensity of the emission was measured by a laser photometer averaging over 100 pulses suppressing the measurement fluctuation at 1–1.5 %, while the spectrum was measured with a monochromator connected to a diode array.

The emission exhibited a narrow spectrum with a maximum at 453 nm, while its intensity *I* was measured for different lengths *L* of the excitation stripe as well as for different MeOH quantities in the solution as shown in Fig. 1. It

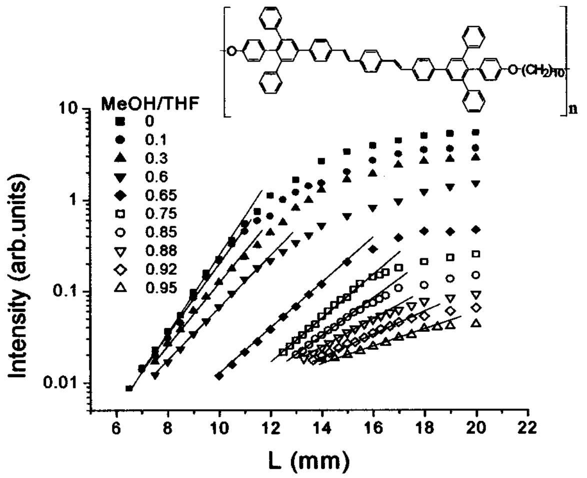

FIG. 1. Output intensity vs excitation stripe length *L* for MeOH/THF solutions of various volume fractions. The solid lines are fits to the data in the unsaturated regime using Eq. (1). The inset shows the chemical structure of the polymer.

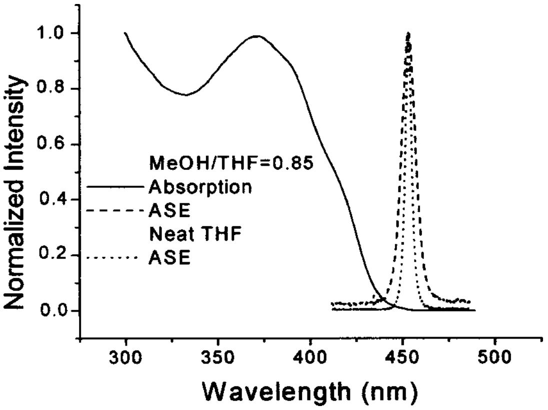

FIG. 2. Absorption and ASE spectra of a polymer solution with a MeOH/THF ratio equal to 0.85 and the ASE spectrum of a neat THF polymer solution.

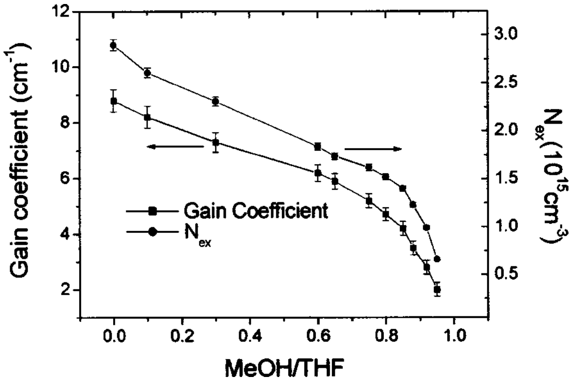

FIG. 3. The gain coefficient g and the excited isolated chains concentration N_{ex} as a function of MeOH/THF. Both exhibit a gradual decrease becoming more intense for MeOH/THF$>$0.65.

can be seen that the emission intensity increases exponentially as far as L is shorter than a critical value L_{sat}. These results are indicative of a typical ASE process.[18,19] L_{sat} is determined as the length where a saturation of the amplification begins and the ASE intensity no longer exhibits an exponential increase. The gain coefficients g are deduced by fitting the data in the unsaturated regime (solid lines in Fig. 1) using the following equation:[20]

$$I = A\{\exp[(g-\gamma)L]-1\}, \tag{1}$$

where A is a geometry-dependent constant and γ the loss coefficient. Measurements of γ, taken by moving the excitation stripe away from the edge of the sample close to the detector and monitoring the output energy,[18] showed that this parameter is negligible. This is valid even for polymer solutions with high MeOH quantity namely for solutions with aggregates indicating that aggregates do not absorb at the ASE wavelength. This is additionally shown in Fig. 2 where the absorption spectrum of a polymer solution with a MeOH/THF ratio equal to 0.85 is depicted together with its ASE spectrum without any overlap between them. In the same figure, the ASE spectrum obtained from a neat THF polymer solution is also shown, indicating that ASE exhibits no red shift by increasing MeOH quantity. The deduced gain coefficients versus the MeOH/THF volume fractions are shown in Fig. 3, indicating a gradual decrease of the gain and this becomes abrupt for high values of the MeOH/THF ratio.

In order to further investigate the mechanism responsible for the gain behavior and especially for high MeOH quantities, SE cross sections (σ_{SE}) were determined in all samples. σ_{SE} is given by

$$\sigma_{SE} = g/\Delta N, \tag{2}$$

where ΔN is the concentration of the population inversion between the excited and the lower laser levels, namely, $\Delta N = N_{ex}\text{-}N_1$. In the case of four-level laser media, such as conjugated polymers, N_1 can be neglected. N_{ex} in our case was determined through ASE considering that a certain excited molecule responsible for this kind of radiation emits only one photon because of the single pass of the light through the sample. Therefore, by counting the total number of the emitted ASE pulse photons from both sides of the sample and dividing by the polymer's quantum yield and the active volume of the excitation stripe, N_{ex} can be determined. The calculations are valid as far as losses due to spontaneous emission and scattering on the sample's sides are neglected. In our case, the ASE pulse energy, emitted from a stripe length equal to the L_{sat} was used. In this critical excitation stripe length, the majority of the excited molecules, responsible for the ASE, contributes to the amplification procedure and the losses due to the spontaneously emitted photons are minimized. The cross sectional area of the excitation stripe is equal to the output beam's cross section exactly at its exit from the sample, and is 0.16 mm^2. The results for N_{ex} are also shown in Fig. 3, exhibiting a similar behavior to the gain. The total experimental error of the N_{ex} values, is ~2%, which mainly originates from the pulse fluctuation of the N_2 laser. The similarity between these two independent sets of measurements (i.e., N_{ex} and gain) especially for high values of MeOH/THF ratio, bearing in mind their experimental errors, clearly denotes the existence of a physical effect in this MeOH/THF ratio regime.

The calculation of σ_{SE} through Eq. (2) has provided the same value, equal to $\sim 3\times10^{-15}$ cm^2, in all solutions with different values of the MeOH/THF ratio. This reaffirms our previous conclusions that ASE radiation originates from the same species i.e the isolated chains existing in both environments. The elimination of SE in aggregates should be attributed to the forbidden radiative transition from the first excited energy state to the ground one. Thus, N_{ex} in Fig. 3 corresponds to the concentration of the excited isolated chains which decreases following an analogous decrease to the total isolated chains.

Based on the previous conclusion that ASE originates only from isolated chains, the procedure of the aggregation is studied using the measured values of N_{ex} shown in Fig. 3. However, the excited isolated chains constitute a fraction of the total isolated ones. This fraction was estimated for the solution without MeOH where all polymer chains are isolated and was found to be 1/230. Considering that this value remains constant for all MeOH/THF ratios, the total concentrations of the isolated chains N_{is} can be obtained by multi-

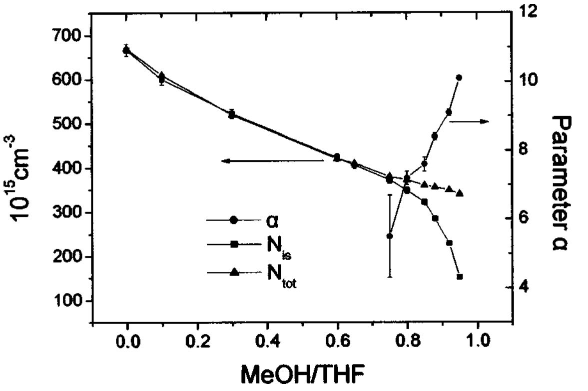

FIG. 4. The isolated chains concentration N_{is} and the total polymer concentration N_{tot} as a function of MeOH/THF. For MeOH/THF$>$0.65, the two curves are separated indicating the formation of aggregates. For these solutions the parameter α is also plotted.

plying the N_{ex} concentration by 230, and the results are shown in Fig. 4 with an uncertainty similar to that of N_{ex} (2%). In the same figure the total concentration of the polymer chains N_{tot} (isolated and aggregated) versus MeOH/THF is also shown indicating a gradual dilution of the polymer because of the MeOH addition. The experimental error for N_{tot} is almost infinitesimal as the quantity of the polymer is measured using an electronic scales. As can be seen in Fig. 4, the curve of the isolated chains N_{is} coincide with the total polymer one N_{tot}, for values of the MeOH/THF ratio up to 0.65. This verifies that for lower MeOH/THF ratios than 0.65 there is no aggregate formation, and consequently all the polymer molecules are in the isolated form. Moreover, the coincidence of the two curves up to MeOH/THF of 0.65, in Fig. 4, constitutes a strong indication that the fraction of the excited to total isolated chains is constant (1/230) according to our previous assumption. For higher values of the MeOH/THF ratio than 0.65 the two curves are clearly separated (bearing in mind their experimental errors) indicating an abrupt reduction of the isolated chains in comparison to the total ones. This means that aggregates are formed and the concentration of the polymer chains contributing to aggregates formation is calculated by subtracting N_{is} from N_{tot}. It is obvious that the critical polymer concentration for aggregation is obtained for the solution with MeOH/THF$=$0.65 and is $(4.10\pm0.07)\times10^{17}$ cm^{-3}. A further affirmation of aggregates formation is that the solutions became turbid for MeOH/THF$>$0.65 with no phase separation. The latter is a strong indication that the aggregates formed are one dimensional. The aggregates formation is therefore the reason for the abrupt decrease of the gain in solutions with MeOH/THF$>$0.65 (Fig. 3).

For a further investigation of the aggregation procedure, a model based on thermodynamic principles is applied. As it was concluded, for MeOH/THF$>$0.65 both isolated and aggregated chains exist in the solutions in dynamic equilibrium. In this case, the total solute concentration C according to molecules conservation is

$$C=X_1+X_2+X_3+\cdots=\sum_{N=1}^{\infty}X_N, \tag{3}$$

where X_N is the concentration of isolated chains involved in aggregates of N chains (X_1 corresponds to the concentration of chains in the isolated form). In Eq. (3), C and X_N are expressed in mole fraction relative to the total solvent moles. Using the law of mass action, X_N is given by the equation[21]

$$X_N=N\{X_1\exp[(\mu_1^0-\mu_N^0)/kT]\}^N, \tag{4}$$

where μ_1^0 and μ_N^0 are the standard parts (i.e the mean interaction free energy per molecule) of the chemical potentials in isolated chains and in aggregates with N chains, respectively. The necessary condition for the formation of aggregates is that $\mu_N^0<\mu_1^0$. In the case where only one dimensional aggregates are formed, μ_N^0 according to the thermodynamic model (Ref. 21), is given by the equation

$$\mu_N^0=\mu_\infty^0+\frac{\alpha kT}{N}. \tag{5}$$

The parameter α is a dimensionless positive constant dependent on the strength of the interchain interactions and μ_∞^0 the mean free energy in an infinite aggregate. Equation (4) using Eq. (5) becomes

$$X_N=N[X_1e^{\alpha}]^Ne^{-\alpha}. \tag{6}$$

After inserting Eq. (6) into Eq. (3), α can be expressed by the form

$$\alpha=\ln\left(\frac{1-\left(\frac{X_1}{C}\right)^{1/2}}{X_1}\right). \tag{7}$$

Finally, the density distribution of molecules in aggregates of N chains is calculated by inserting Eq. (7) into Eq. (6) yielding the equation

TABLE I. The calculated values of C, X_1 and α. The uncertainty of X_1 is 2% (similar to N_{ex}), while the uncertainty of α is estimated by error propagation.

MeOH/THF	0.75	0.8	0.85	0.88	0.92	0.95
$C(10^{-5})$	3.6	3.5	3.4	3.3	3.2	3.2
$X_1(10^{-5})$	3.54	3.2	3.0	2.6	2.1	1.4
α	5.5±1.2	7.2±0.2	7.6±0.2	8.4±0.1	9.1±0.1	10.10±0.04

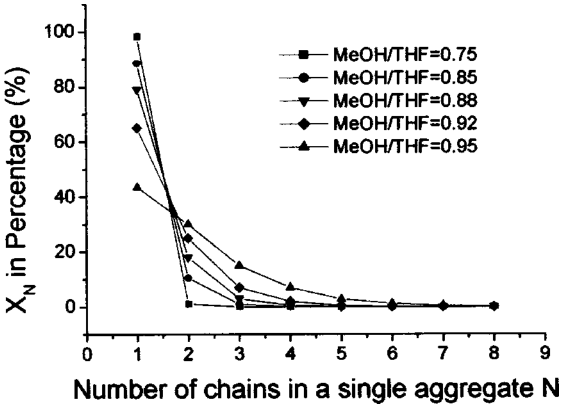

FIG. 5. The distribution of polymer chains X_N in percentage as a function of the aggregation number N for values of MeOH/THF >0.65, where aggregates are formed.

$$X_N = N X_1 \left(1 - \sqrt{\frac{X_1}{C}} \right)^{N-1}. \tag{8}$$

The application of this thermodynamic model in our case requires the conversion of N_{is} and N_{tot} concentrations (expressed in units of cm^{-3}) depicted in Fig. 4 in dimensionless mole fraction units relative to the total solvent moles ($\mathrm{moles}_{\mathrm{THF}}+\mathrm{moles}_{\mathrm{MeOH}}$) becoming X_1 and C respectively. The calculated values of X_1 and C are given in Table I for MeOH/THF$\geqslant 0.75$. In the same table the values of parameter α calculated from Eq. (7) are given and are also shown in Fig. 4 with their experimental error calculated by error propagation. It is observed that α increases with the MeOH/THF ratio indicating a worsening of the solvent quality and an increment of polymer-polymer interactions.

The X_N distributions calculated through Eq. (8), for MeOH/THF$\geqslant 0.75$, are shown in Fig. 5 offering a quantitative description of the gradual transition of the polymer molecules from the isolated to the aggregated state. As MeOH/THF increases, less polymer chains remain isolated while more of them form aggregates. The number of chains involved in aggregates of a specific size decreases as aggregates become larger incorporating up to seven chains for MeOH/THF$=0.95$. The aggregates mainly consist of a small number of polymer chains indicating that they are one-dimensional in accordance to our previous statement.

The distributions in Fig. 5 are obtained in our case using ASE. Neither fluorescence nor laser radiation can be used for studying the aggregation procedure. In particular, fluorescence cannot be utilized since the emitted photons originate from both isolated and aggregated chains. Moreover, the light lacks directionality and the emitted photons cannot be gathered. On the other hand, laser radiation has directionality as well as emission originating from the isolated chains but because of many passes of the light through the sample, a certain isolated chain emits an unknown number of photons. Additionally, the monitoring of N_{ex} in the aggregated solutions, as done through ASE, cannot be realized using absorption techniques since both isolated and aggregated chains simultaneously absorb the pumping photons and the contribution of these two species on the absorption cannot be distinguished. All the above lead to the conclusion that ASE is the only mechanism that can reveal the procedure of aggregation because it originates only from the isolated chains and a certain chain emits only one ASE photon. Besides, the directionality of the light permits easily its measuring by a simple detector.

In conclusion, the optical gain and SE cross section in isolated and aggregated chain environments were measured by systematically changing the fraction of poor/good solvent in polymer solutions. It was proved that ASE originates from isolated chains existing in both environments confirming our previous spectroscopic results. Aggregates are formed for a poor/good solvent ratio higher than a critical value and they substantially suppress the gain. Based on ASE results and a thermodynamic model, the critical polymer concentration for aggregation, the strength of the intermolecular interactions (α), as well as the distributions of polymer chains in aggregates (X_N), were determined.

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