JOURNAL OF MATERIALS SCIENCE 26 (1991) 5770–5776

Laser induced non-linear thermochemical processes in polymers

L. I. KALONTAROV, R. MARUPOV
S. U. Umarov Institute of Physics and Engineering, Tajik SSR Academy of Sciences, Akademgorodok, Dushanbe 734063, USSR

Laser induced thermochemical processes in the thin films of polyvinyl alcohol (PVA) and polyacrylnitrile (PAN) had been studied. It was found that the laser thermodehydration of PVA had three stages: the activation stage, the stage of thermochemical instability and the stationary one. Such process dynamics can be explained by the alteration of positive and negative feedback between thermal and chemical degrees of freedom. There was shown, theoretically and experimentally, the possibility of spontaneous formation of spatially-inhomogeneous structures during the process of laser dehydration of PVA due to inhomogeneity of the laser heating. It was also found that the non-linear dynamics of laser chemical reactions influence the laser stability of PAN leading to an unexpected dependence of the last one on the polymeric film thickness.

1. Introduction

Recently, investigations on the thermochemical effect of laser radiation were considerably developed [1–7]. It is due to a high capability of chemically active systems to reveal self-organization phenomena in the laser thermal field. The existence of feedback between thermal and chemical degrees of freedom is the main peculiarity of laser heating which, to a great extent, stimulates the above mentioned phenomena. As the heating rate depends on the absorbed radiation intensity and the absorption characteristics of the system can be changed during chemical reaction, so the temperature and concentration variations become interrelated through the parameters of laser radiation. To add the non-equilibrium and non-linear character of the current processes, due to permanent energy inflow on account of the laser effect, and the chemical reaction rate's non-linear dependence on the temperature gives a system which is "chemically active media-laser radiation" with all the conditions necessary for different spatio-temporal regimes of thermochemical transformations [8]. In particular, the phenomena of laser chemical bistability and travelling waves propagation were observed [3–5], oscillating regime and generation of spiral waves during laser combustion of metals were found [6, 7].

Using the laser radiation monochromaticity the heating energy may be introduced *via* a selected component of the reaction. Such selectivity leads to absolutely different types of dynamic behaviour of the systems upon the shifting of the radiation wavelength from one reagent to another. Here it is essential that the radiation power plays a role of transmission coefficient in the channel of feedback and it gives an opportunity to control the system behaviour by changing the power.

Until now the laser macrokinetics of quite a limited range of objects was studied experimentally, among them being no works on the stimulation of reactions within solid polymers. However a great variety of macromolecules thermochemical reactions and numerous literature data [9, 10] confirm that such investigations would be promising. This present paper offers the results on experimental and theoretical study of the non-linear effects initiating upon laser heating of some polymeric systems.

2. Experimental procedure

As the dynamics of thermochemical transformations in the laser radiation field is defined by the absorbing components of the reaction, the polymer absorptivity on the laser wavelength and its dependence on the irradiation time have been taken as the principal object of the observation. Schematic of the apparatus is given in Fig. 1. Polymer samples in the form of thin films 35 and 60 μm thickness were subjected to continuous radiation of Ar-laser with a wavelength of 514.5 nm (a). The diameter of the incident beam was

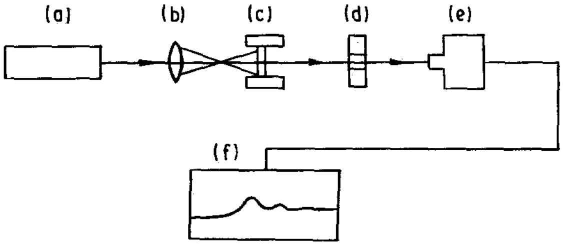

Figure 1 Scheme of experimental apparatus: (a) laser, (b) lens, (c) holder with a sample, (d) diaphragm, (e) laser power measuring unit, (f) recorder.

0022-2461/91 $03.00 + .12

regulated by means of lens (b), thus selecting the necessary area of irradiation. Photometry of the radiation passing through the sample was measured by a power measuring unit (e) connected with the recorder (f). Diaphragm (d) served for the beam central part selection. The kinetics of polymer films absorptivity changes at the laser wavelength was measured to control the accumulation of the reaction absorbing products.

The polymers with a known mechanism of thermodegradation, the products of which absorb within the visible range of the spectrum and consequently radiation of Ar-laser have been taken as the objects of investigation. Polyvinyl alcohol (PVA) and polyacrylnitrile (PAN) have been studied. PVA films were obtained from a 10% water solution of the polymer. To accelerate the process of PVA thermodehydration into polymer solution prepared for film founding, 1 $\mathrm{mol\,l^{-1}}$ of HCl (4 ml of the acid for 20 ml of the polymer) was added. The acid is a catalyst for PVA dehydration and even a little heating of the polymer leads to its dehydration. As a result, in the main and side chains of macromolecules some conjugated polyene appeared, which are efficiently absorbing within visible spectral range.

The films of the studied PAN were obtained from a 5% solution of the polymer in dimethyl formamide. The initial polymer is transparent within visible spectral range. PAN heating leads to the formation of polyconjugated structures of different types, resulting in its colouring. The polyconjugated structures are the result of processes of intra and inter-chain cyclization, the mechanism of which is not known in detail.

3. Results and discussion

3.1. Self-stabilization of PVA laser dehydration process

Visually laser heating of PVA results in its colouring, indicative of the thermodehydration reaction and polyenic areas formation. The kinetic curves (Fig. 2) show that PVA laser dehydration process is characterized by an activation period at the finish of which some avalanche like acceleration of the reaction takes place and the so called thermochemical instability (TCI) is being developed. The following dynamics of the process depends on the intensity of the radiation and the thickness of the polymeric film. If the intensity is high, then after TCI a carbonization takes place, in this zone the polymer starts to burn and the fracture of the film is being produced (curve (a), Fig. 2). After decreasing the intensity and/or sample thickness the dehydration reaction is slowing down just after TCI and starts tending to some stationary state, characterized by definite values of temperature and concentrations of absorbing products (curve (b), Fig. 2).

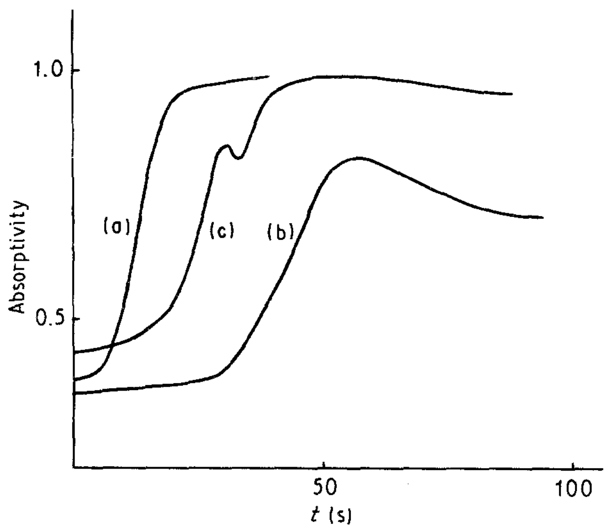

Figure 2 Dependence of PVA absorptivity in the centre of laser beam on the time of irradiation. (a) $I = 0.66\ \mathrm{W\,cm^{-2}}$, $d = 53\ \mu\mathrm{m}$, (b) $I = 0.49\ \mathrm{W\,cm^{-2}}$, $d = 36\ \mu\mathrm{m}$ (c) $I = 0.50\ \mathrm{W\,cm^{-2}}$, $d = 55\ \mu\mathrm{m}$.

To explain the observed facts it is necessary to consider the PVA thermodehydration process in more detail. It is known [11] that isothermal heating of PVA samples, especially in the presence of catalysts, results in their colouring due to absorption of light by dehydration process products. In the course of the conducted experiments on PVA films isothermal heating within the temperature interval of 340–450 K, the samples were coloured brown, the colour becoming more intensive through the thermoprocessing period. In [12] the effect of thermal clarifying of dehydrated PVA was revealed. It was found that in the dynamic heating of PVA films their absorptivity within the visible spectral range is increasing at first (formation of polyenic areas is under way) and then decreases at a certain temperature (500–520 K), so the clarifying of the samples is being observed. The authors of [12] think this effect to be the result of polyene degradation due to the high temperature. Starting from the above, the change in concentration of PVA products absorbing within the visible spectral range and consequently the Ar-laser radiation may be described by the following equation

$$\begin{aligned} \mathrm{d}c/\mathrm{d}t &= v_1 \exp(-E_1/RT) - cv_2 \exp(-E_2/RT), \\ c(0) &= c_1 \end{aligned} \qquad (1)$$

where c is the relative concentration of absorbing products, v_1, E_1 and v_2, E_2 are the pre-exponential multipliers and activation energies for reactions of accumulation and decay of the absorbing products, $E_2 > E_1$.

Now let us imagine that a laser radiation beam uniform in the cross-section falls on some initial PVA film. It is evident that the mechanism of the positive feedback between the rate of the polyene accumulation and the temperature defined by the absorbed radiation intensity has to start soon. Consequently the PVA dehydration process will be sharply accelerated and TCI will be developed. But at the certain temperature the effect of thermal clarifying will appear, the sign of the feedback will change and self-stabilization of the process will tend to some stationary state. The experimental kinetic curve obtained for the polymer absorptivity characterizing the change of the absorbing products concentration (curve (b), Fig. 2) confirms such conclusions. The process of laser heating of thermally thin polymeric film will be expressed by the equation of the thermal balance

$$\mathrm{d}T/\mathrm{d}t = \frac{Ikc}{c_p\rho} - \frac{\mathrm{h}}{c_p\rho d}(T - T_a),\ T(0) = T_0 \qquad (2)$$

where T is the temperature, k is the coefficient of absorption, I is the intensity of radiation, h is the heat exchange constant, c_p, ρ, d are the specific heat, density and thickness of the polymeric film, respectively, T_a is the ambient temperature. In determining Equations 1 and 2 it was assumed that polyene resonantly absorbing radiation transduce the absorbed energy to the environment in a non-radiative way and the last one is heated. In this case the duration of non-radiative relaxation was considered to be much less than the characteristic time of the chemical reaction and consequently excluded the process occurrence according to the photochemical mechanism. As we were interested in the qualitative aspect of the PVA laser dehydration process depending on the parameters of the problem we did not take into account Beer's character of absorption and assumed the polymer concentration to be constant and equal to 1. For convenience in analysis we rewrote Equations 1 and 2 in non-dimensional variables

$$\begin{aligned} \mathrm{d}c/\mathrm{d}\tau &= m\exp(-\,\nu/y) - c\exp(-\,1/y) = P(c, y) \\ \mathrm{d}y/\mathrm{d}\tau &= pc - \mu(y - y_a) = Q(c, y) \qquad (3) \end{aligned}$$

where

$$y = \frac{R}{E_2}T,\quad y_a = \frac{R}{E_2}T_a,\quad \tau = v_2 t,\quad m = \frac{v_1}{v_2}$$

$$p = \frac{\mathrm{R}kI}{E_2 v_2 \rho c_p},\quad \nu = \frac{E_1}{E_2} < 1,\quad \mu = \frac{\mathrm{h}}{v_2 c_p \rho d}$$

Setting the right hand side of the Equation 3 equal to zero we have found that the system has a single stationary state to which the stationary values of concentration and temperature c_s and y_s correspond. Following [13] let's study its stability in terms of the theory of non-linear oscillations. In accordance with the first method by Liapunov the equilibrium state in the system of two non-linear differential equations is stable when the following conditions are fulfilled

$$\begin{aligned} \delta &= -(a + d) > 0 \\ \Delta &= da - bc > 0 \end{aligned} \qquad (4)$$

where $a = P'_c(c_s, y_s)$, $b = P'_y(c_s, y_s)$, $c = Q'_c(c_s, y_s)$, $d = Q'_y(c_s, y_s)$ are the coefficients of functions $P(c, y)$ and $Q(c, y)$ decomposition into Taylor's law in the vicinity of the equilibrium state. It is easy to verify in our case, that Conditions 4 are fulfilled and consequently the stationary state of Equation 3 is a stable node or a focus. Using the Bendikson's criterion we can show that there are no limit cycles in the system and this means that oscillations are impossible. Thus in some time the process of PVA laser dehydration has to relax to stationary values of c_s and y_s. These values essentially depend on problem parameters. Fig. 3 shows the nullclines for Equation 3 intersection of which corresponds to the stationary state. It is seen from the figure that changing p and μ parameters (these very parameters were varied in the course of experiment) we can obtain different values of c_s and y_s. So the increase of the radiation intensity p leads to an increase of the stationary temperature y_s, the value of which can exceed the temperature y_c necessary for the beginning of carbonization and we obtain curve (a) in Fig. 2. At lesser intensity and/or thickness of the polymeric film (this is equivalent to an increase of μ) when $y_s < y_c$ and the process obeys Equation 3 we observe the kinetic curve (b) in Fig. 2.

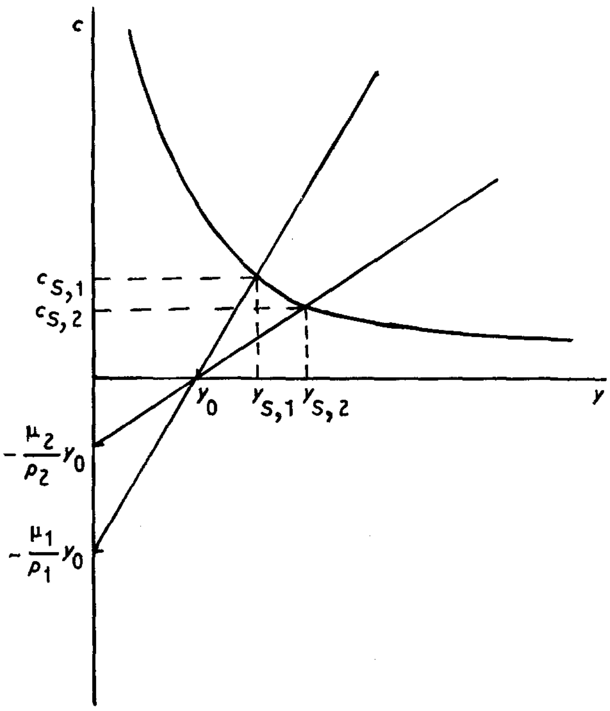

Figure 3 Nullclines for Equation 3.

Thus in spite of the fact that both, usual dynamic heating and laser heating finally lead to the same results (first the increase of polyene areas concentration and then to their degradation), nevertheless the dynamics of the PVA thermodehydration process has a principle difference between the two types of heating. In the first case it is defined by the heating rate and in the second it is due to the internal characteristics of the system "laser radiation-chemically active polymer" itself because of the feedback between the thermal and chemical degrees of freedom. Varying the radiation intensity and/or the film thickness we change the transmission coefficient in the feedback channel and consequently have an opportunity to control the process of PVA dehydration.

3.2. Formation of spatial structures in PVA laser dehydration

Until now we considered PVA reaction in the laser radiation field to be synchronous throughout the whole irradiated surface and described the process dynamics by determenistic equations, which on the whole adequately reflect the kinetics of the change of the polymer absorptivity in the centre of the laser beam. But it is evident, that heating of the polymer film is non-uniform due to a definite intensity distribution along the laser beam cross-section. This nonuniformity of heating leads to an asynchronous response of the spatially distributed points of the polymer and the temperature gradient emerging in this case may cause thermodiffusive flows of reagents.

In a general case, a mathematical description of the laser heating of the chemically active system consists of the equations of the heat conductivity with laser heat source and diffusion and kinetics of the reaction components absorbing the radiation. In our case, taking into account the small thickness of the polymer film and that mostly $I(r) = I_0 \exp(-r^2/r_0^2)$ we can confine the problem to planar type with the radial symmetry

$$\frac{1}{\chi}\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{1}{\chi}Q(c, T), \quad T(0) = T_0$$

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{D_1}{D}\frac{1}{T}\frac{\partial T}{\partial r}\right) + \frac{1}{D}P(c, T), \quad c(0) = c_1$$

$$\left(\frac{\partial T}{\partial r}\right)_{r=0,\,R=0}, \quad \left(\frac{\partial c}{\partial r}\right)_{r=0,\,R=0} \qquad (5)$$

where r is the distance from the laser beam centre, χ, D, D_1 are the coefficients of the temperature conductivity, diffusion and thermodiffusion, respectively, R is the full radius of the radiation beam, $P(c, T)$ and $Q(c, T)$ are Equations 1 and 2, respectively, considering only that in $Q(c, T)$ unlike Equation 2 $I = I(r)$. As the homogeneous problem of Equation 5 (Equation 3) has the single stable state of the current equilibrium then according to the general theory of such equations [14, 15] within the given system two types of spatial effects can be observed. They are the relaxation wave and thermodiffusion instability. Both effects were observed experimentally.

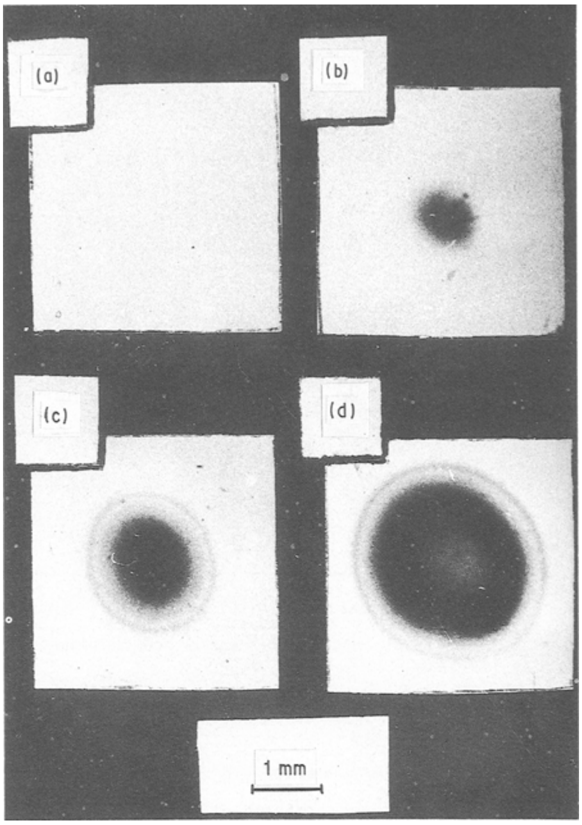

Figure 4 Micrographs representing the process of generation and propagation of relaxation wave.

Let's first consider the relaxation wave which transforms the system from the metastable state to the stationary one. Fig. 4 presents micrographs showing the process of generation and propagation of this wave. It can be seen that the dehydration reaction begins in the centre of the laser beam and then in a ring-like shape, propagates to the periphery until it has the pattern shown in Fig. 5. Simultaneously the kinetic curve of the absorptivity in the centre of the laser beam (curve (b) in Fig. 2) sharply increases first and then relaxes to the stationary state.

According to the micrographs (Fig. 4) and kinetic curve the concentration relaxation wave front may be

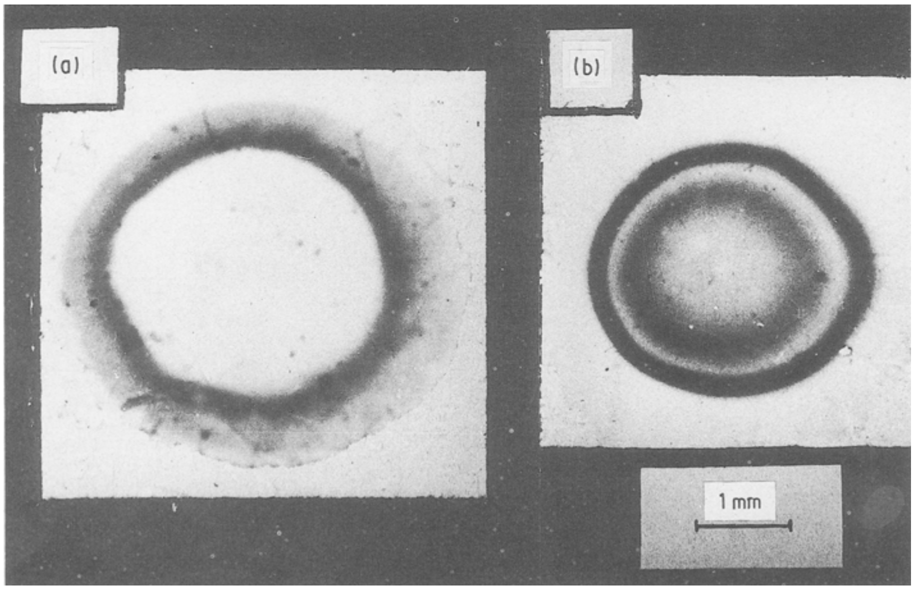

Figure 5 Micrographs of spatial structures forming during the process of PVA laser dehydration.

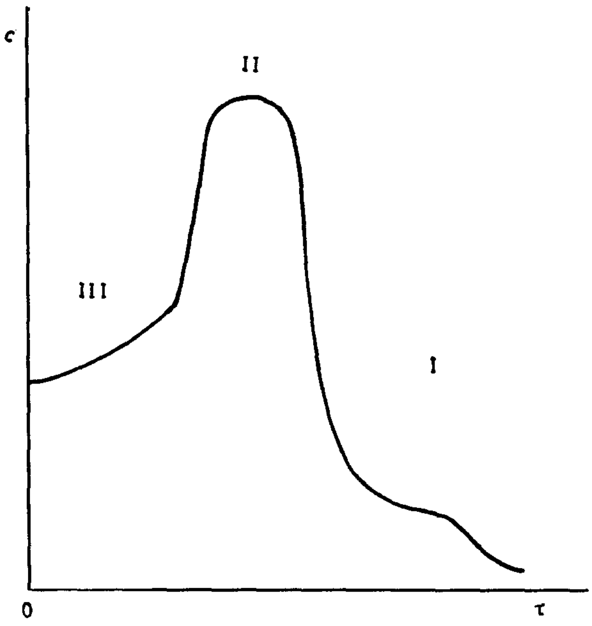

Figure 6 Scheme of the front of relaxation concentrational wave.

conditionally divided into three zones having a specific colour, the intensity of which characterizes the concentration of the absorbing products (Fig. 6): I is the activation zone or the zone of slow reaction and has a yellow colour, II is the zone of TCI and has a brown colour and III is the zone of relaxation and has a weak-yellow colour. It should be noted that the wave front stops not having achieved the edges of the radiation beam, i.e., at some distance from the laser beam centre r_s the relaxation wave failure occurs. This distance depends on radiation intensity increasing linearly with the increase of the last one (Fig. 7). The reason of the relaxation wave generation is quite obvious.

As TCI activation time significantly decreases with radiation intensity increase [16] the dehydration reaction begins firstly in the centre of the laser beam where the intensity is maximum (Fig. 4b). The temperature in the beam centre becomes higher, and as a consequence of the heat conductivity, the temperature of zones adjacent to the centre also increases, that accelerates TCI development within the zones. Thus the reaction begins to propagate from the centre to periphery (Fig. 4c and d). After TCI polyene concentration begins to decrease and tends to the stationary state we can observe the relaxation concentration wave schematically shown in Fig. 6. At some distance from the beam centre the intensity $I(r)$ decreases up to such value I_{min}, that the heat conductivity effects can not insure the TCI development and further reaction propagation and as a result the wave failure is observed. It is obvious that when intensity $I(r)$ increases the value I_{min} will be achieved at larger distances, r_s. As a whole the given wave has the same nature as other types of travelling chemical waves and consequently possesses the properties inherent to such waves. In particular the interaction of two such waves leads to their mutual annihilation (Fig. 8b).

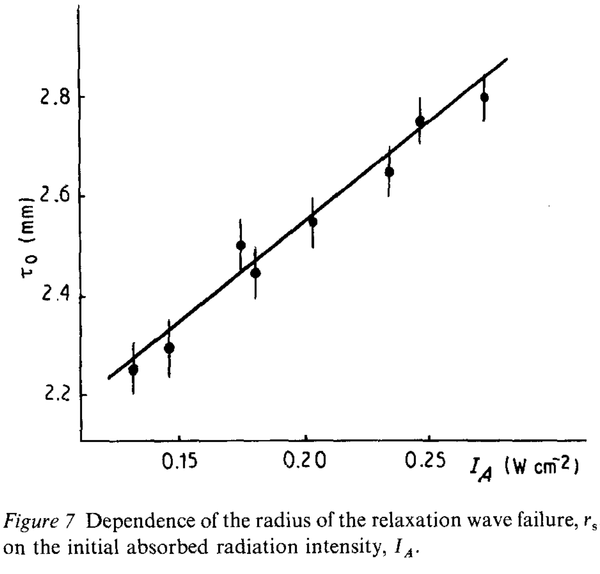

Figure 7 Dependence of the radius of the relaxation wave failure, r_s, on the initial absorbed radiation intensity, I_A.

As was mentioned above, on laser PVA dehydration one more type of spatial instability can be observed. Unlike the relaxation wave this instability appears when the intensity achieves some threshold value. According to the kinetic curve (curve (c) in Fig. 2) it follows that the instability under consideration also initiates within the central part of the laser beam, but after the relaxation wave has passed. Then it moves towards the periphery in a ring-like shape and not having achieved the relaxation wave, stops. The stationary pattern is shown in Fig. 5b. The distance from the beam centre at which the stop of the moving structure occurs also depends on the laser radiation intensity (Fig. 8a). The colour of the second spatial structure is red-orange.

Based on the model in Equation 5 the only reason for the forming of such an instability can be the absorbing component thermodiffusion phenomenon. In [17, 18] the thermodiffusion instability upon laser heating of gases was studied and it was shown that a necessary condition for its formation is the intensity exceeding some threshold value, that is characteristic

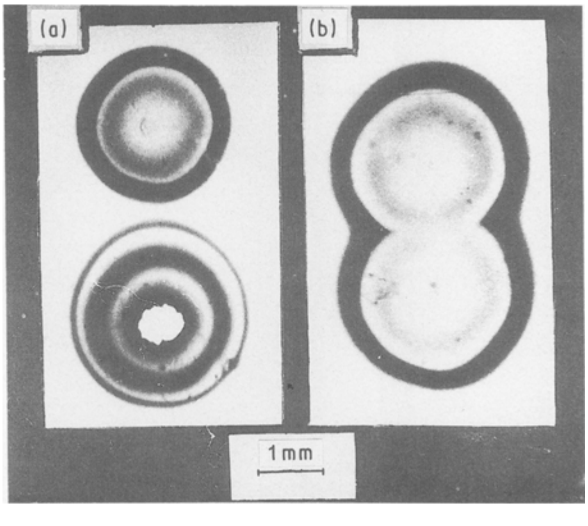

Figure 8(a) Micrographs of spatial structures before (above) and after (below) sharp increase of the radiation intensity (dark and light spots in the centre of micrograph below are due to carbonization and film fracture), (b) superposition of the two structures.

for the case under discussion. As a whole, the mechanism of development for the thermodiffusion instability upon PVA laser dehydration can be shown like this. As the stationary values of the temperature and concentration of absorbing products depend significantly on the radiation intensity, their distribution within the relaxation zone will be inhomogeneous. The temperature will be maximum in the centre of the beam where $I(r)$ is maximum. When r is increased temperature will decrease rather sharply. The inverse relation is characteristic for the stationary concentration. Thus within the relaxation zone there is quite a strong temperature gradient which at some appropriate intensity will disturb the stationary temperature and concentration distribution and cause the absorbing component thermodiffusion flow to move towards the hotter zone, i.e. towards the beam centre. As a result the concentration of the absorbing reagents in the beam centre increases, this causes the additional absorption of the laser radiation and consequently the increasing of the temperature. This, in its turn, causes the dehydration of unreacted parts of the polymer matrix and, in the long run, the development of a new TCI (curve (c) in Fig. 2) and its further self-stabilization and propagation rather according to the same scheme as in case of the relaxation wave. Thus the form of the new structure is exactly the same as the relaxation wave structure form (Fig. 5b). As a result of the decrease of concentration of the unhydrated part of the polymer matrix after the relaxation wave passing, the depth of the thermodiffusion instability development is significantly lower, which can explain the weaker (red-orange) colour of it. The earlier stop, while thermodiffusion instability propagates towards the periphery is caused by the decrease of the reaction rate because of the expenditure of the original polymer, concentration of which diminishes when the distance from the beam centre increases.

3.3. The role of non-linear effects in laser destruction of polymers

A significant role of the TCI in optical fracture initiation in the polymers has been shown [16, 19, 20]. Nevertheless as it is seen from the materials mentioned above the dynamics of the thermochemical transformations of polymers in the laser radiation field is not limited by TCI. Other regimes of the reactions, naturally, influence the polymer laser stability, sometimes accelerating and sometimes slowing the destruction process. Thus in case of PVA, the presence of the stable stationary state to which the process of the laser thermodehydration relaxes, should lead to a sharp increase in the polymer laser stability, that which we observe at low intensities (curve (b) in Fig. 2). At higher intensities the development of the thermodiffusion instability again initiates destruction, resulting in carbonization and film fracture. Thus spatial inhomogenity of the beam results in polymer laser stability decrease.

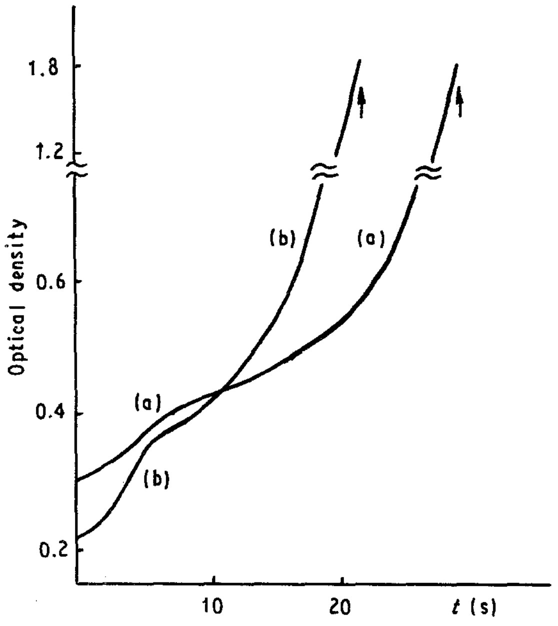

Figure 9 PAN optical density at the laser wavelength dependence on the irradiation time. (a) $I_{a,0} = 0.61\ \mathrm{W\,cm^{-2}}$, $I_{a,1} = 0.705\ \mathrm{W\,cm^{-2}}$, $d = 60\ \mu\mathrm{m}$; (b) $I_{a,0} = 0.51\ \mathrm{W\,cm^{-2}}$, $I_{a,1} = 0.73\ \mathrm{W\,cm^{-2}}$, $d = 45\ \mu\mathrm{m}$. Arrows show at the moment of film fracture.

Let us see how the non-linear effects influence the laser destruction of PAN, leading to the unusual dependence of the polymer laser stability on the film thickness. According to the kinetic curves of destruction for thick and thin PAN films the last one has less stability (Fig. 9) in spite of the fact that the initial value of the absorbed radiation intensity $I_{a,0}$ (which determines the activation time of TCI [16]) in this case was less. As follows from the figure the laser degradation of PAN is characterized by two TCI. This fact reflects the complex character of the polymer thermodegradation processes, during which two types of absorbing products appear, their formation being simultaneously, but occurring by different rates. After the first TCI formation the reagents, under which influence it was developed, are destroyed (otherwise the second instability could not appear) and further accumulation of the absorbing products and the whole process of the PAN laser destruction is determined by the second absorbing component, giving the next TCI leading to carbonization and optical fracture of the polymer.

According to the experiment the dynamics of the laser chemical transformations of PAN without taking into account heat conductivity and reagent expenditure will be described by the following equations

$$\begin{aligned} \mathrm{d}c_1/\mathrm{d}t &= v_1 \exp(-E_1/RT) - c_1 v_1^* \exp(-E_1^*/RT) \\ \mathrm{d}c_2/\mathrm{d}t &= v_2 \exp(-E_2/RT) \qquad (6) \\ \mathrm{d}T/\mathrm{d}t &= \frac{I(k_1c_1 + k_2c_2)}{\rho c_p} - \frac{\mathrm{h}}{\rho c_p d}(T - T_a) \end{aligned}$$

The indices 1 and 2 relate to the first and the second absorbing components, respectively. The TCI activation time exponentially depends on the activation energy of the absorbing products accumulation process [16] therefore under the laser action on PAN, firstly an instability develops on the absorbing products, the formation of which occurs at a lower activation energy, i.e., $E_2 > E_1$. For the intensity interval studied the activation time of the first TCI is small and does not depend significantly on the latter. In this case the concentration c_2 can be assumed as being constant, to exclude the second equation from the Equation 6. The equations obtained coincide with those earlier studied for the laser thermodehydration of PVA and consequently the kinetics of the concentration change for the absorbing products of the first type should coincide qualitatively with curve (b) in Fig. 2. The development of the first TCI leads to the absorbed radiation intensity increase and, respectively, to the temperature raise, that causes the accelerated formation of the second absorbing product and activation time decrease of the next TCI. The development degree of the first TCI is determined by the stationary concentration, $c_{1,s}$ the value of which decrease when the film thickness increases (Fig. 3) and it can be seen from the experiment (in Fig. 9 the relation of the optical density to the film thickness is equal 65 cm^{-1} for the first curve and 80 cm^{-1} for the second one). Therefore although the initial absorbed radiation intensity $I_{a,0}$ was less for thinner film (Fig. 9), the absorbed radiation intensity after the first TCI $I_{a,1}$ for this film was higher than that for the thick one. Consequently the second TCI activation time and the laser stability itself of the thin PAN films is less than that of thick films, when other conditions are the same.

Another interesting conclusion based on the data obtained is the possibility of solution for the inverse problem, that is to judge the polymer thermodegradation using the laser experiment data. As TCI activation time strongly depends on the kinetic parameters of the thermodegradation, the proceeding processes during usual simultaneous heating in the case of laser influence become time separated. What concerns PAN the first two equations of Equation 6 obtained from the laser chemical experiment analysis, in fact reflect the process of the polymer thermodegradation and can be useful for studying its mechanism. As was found [21] the isothermal decomposition of PAN at the temperature 530 K is followed by a parallel formation of the polyene and polyimine structures. Note that both these types of the conjugated systems effectively absorb within the visible spectral range and consequently our conclusions on PAN thermodegradation find an indirect confirmation in Reference 21.

References

1. F. V. BUNKIN, N. A. KIRICHENKO and B. S. LUK'YANCHUK, *Usp. Fiz. Nauk* **138** (1982) 45.
2. E. C. ZIMMERMAN, M. SHELL and J. ROSS, *J. Chem. Phys.* **80** (1984) 720.
3. *Idem, ibid.* **81** (1984) 1327.
4. J. KRAMER and J. ROSS, *J. Phys. Chem.* **90** (1986) 923.
5. J. KRAMER, J. REITER and J. ROSS, *J. Chem. Phys.* **84** (1986) 1492.
6. V. A. BOBYRIOV, F. V. BUNKIN, N. A. KIRICHENKO, B. S. LUK'YANCHUK and A. V. SIMAKIN, *Kvant. elektronika* **10** (1983) 793.
7. D. T. ALIMOV, V. A. BOBYRIOV, F. V. BUNKIN and B. S. LUK'YANCHUK, *Izv. AN SSSR Ser. Fiz.* **51** (1987) 1144.
8. A. M. ZHABOTINSKY, "Concentration selfoscillations" (Nauka, Moscow, 1974) p. 48.
9. N. V. KARLOV, E. K. KARLOVA, N. A. KIRICHENKO, B. S. LUK'YANCHUK, O. V. NEKLYUDOVA, I. YA. RAVICH, A. N. SAPETSKY and T. N. TOROPTSEVA, *Kvant. elektronika* **9** (1982) 2049.
10. A. P. ALEKSANDROV and N. M. BITYURIN, *Zh. Tekhn. Fiz.* **58** (1988) 1350.
11. C. A. FINCH, in "Polyvinyl Alcohol" (Wiley, New York, 1973) p. 84.
12. M. Z. GAVRILOV, R. N. SVIRIDOVA and I. N. YERMOLENKO, *Zh. Prikl. Spektroskop.* **44** (1986) 435.
13. A. A. ANDRONOV, A. A. VITT and S. V. KHAIKIN, in "Theory of nonlinear oscillations" (Fizmatgiz, Moscow, 1959).
14. YU. A. VASILIEV, YU. M. ROMANOVSKY and V. G. YAKHNO, *Usp. Fiz. Nauk* **128** (1979) 625.
15. YU. M. ROMANOVSKY, N. V. STEPANOVA and D. S. CHERNYAVSKY, in "Mathematical biophysics" (Nauka, Moscow, 1984) p. 25.
16. L. I. KALONTAROV, R. MARUPOV and N. S. ABDULLOEV, *Khim. Fizika* **6** (1987) 1380.
17. F. V. BUNKIN, N. A. KIRICHENKO, B. S. LUK'YANCHUK and YU. YU. MOROZOV, *Kvant. elektroniks* **10** (1983) 2136.
18. F. V. BUNKIN, N. A. KIRICHENKO and B. S. LUK'YANCHUK, *Izv. AN SSSR Ser. Fiz.* **48** (1984) 1485.
19. M. A. LIBERMAN and M. I. TRIBELSKY, *Zh. Experim. Teor. Fiz.* **74** (1978) 194.
20. A. V. BUTENIN and B. YA. KOGAN, *Zh. Tekhn. Fiz.* **49** (1979) 870.
21. O. A. ANDREEVA, YU. N. TOLPAROV and E. I. FIRSOV, *Vysokomol. Soedin.* **28B** (1986) 111.

Received 2 July 1990
and accepted 28 February 1991