polymer reports

The changes in the apparent activation energies of direct current conductivity during radiation curing of unsaturated polyester resins

Irina Pucić Miličić and Franjo Ranogajec
Ruđer Bošković Institute, 41000 Zagreb, POB 1016, Croatia
(Received 14 March 1991; revised 24 August 1991)

Two different apparent activation energies of the direct current electrical conductivity of polyhexandiolmaleate resins, with and without styrene, were determined in the range between 290 K and 350 K. The temperature at which the activation energy change was detected, was assigned to the upper liquid–liquid transition, T_{lp}, where the intramolecular short range local ordering based on hydrogen bonding disintegrated. No effect by the degree of the radiation crosslinking on the T_{lp} transition proved its intramolecular nature. Increasing the radiation crosslinking dose resulted in an increase in the apparent activation energies up to the vitrification dose which was directly dependent on the maleate content.

(**Keywords: unsaturated polyester resins; apparent activation energies of direct current conductivity; liquid–liquid transition; radiation crosslinking; vitrification dose**)

INTRODUCTION

The electrical conductivity of unconjugated polymer systems is very low and predominantly ionic[1]. Ionic current carriers may arise from molecular and atomic ions: impurities, catalysts, additives, etc. Their mobility is inversely proportional to the microviscosity of the polymeric medium and the conductivity exponentially increases with temperature:

$$\sigma = \sigma_0 \exp - (E_a/RT) \qquad (1)$$

The apparent activation energy of the conduction process can be calculated from the slope of the semilogarithmic plot of direct current (d.c.) conductivity *versus* inverse temperature. It may change if there exists any type of physical transformation that influences microviscosity. Also, chemical changes such as crosslinking or degradation of polymeric systems affect microviscosity and the apparent activation energy of the conduction process.

In this work, the temperature dependence of the d.c. conductivity of the unsaturated polyester resins, polyhexandiolmaleates, cured by γ-radiation to different degrees of crosslinking was investigated. Two apparent activation energies of the d.c. conductivity of the unsaturated polyester resins in cases with and without styrene were determined between 290 K and 350 K, in the temperature range above the glass transition temperature (T_g).

EXPERIMENTAL

The changes in d.c. electrical conductivity of polyhexandiolmaleate (PHM) resins were investigated. Depending on the synthesis temperature, the different maleate to fumarate ratios in PHM resin can be obtained, in this case 51, 76 and 90% maleate (the maleate to fumarate ratio is 1:1, 3:1 and 10:1, respectively).

The resin sample was poured into a coaxial cylindrical cell made of alumina with a Teflon top and bottom. The voltage was supplied by an Iskra M 1077 rectifier to the outer alumina cylinder that served as an anode. The interelectrode separation was 2 mm and the d.c. electrical field strength was 5 kV m^{-1}. The current was recorded at the inner cylindrical electrode by a Keithley 619 electrometer.

The experiments were performed in the temperature range between 290 K and 350 K. After thermal equilibrium had been achieved at each temperature, the current was recorded and then the temperature was increased in steps of 3–4 K.

Radiation crosslinking was performed in a ^{60}Co γ-source (dose rate $\sim$3 kGy h^{-1}) at room temperature in steps of 1 kGy (2 kGy for PHM without styrene). After each irradiation, the d.c. conductivity *versus* temperature dependence was measured in the same temperature range.

RESULTS

The Arrhenius type plot of the data collected for the temperature dependence of the d.c. conductivity exhibited two linear parts (*Figure 1*). The apparent activation energy was calculated from the slope of each linear part. At higher temperatures the apparent activation energy is lower than at lower temperatures. The change in d.c. conductivity apparent activation energy of the PHMs under consideration is $\sim$310 K, in the temperature range well above the T_g ($\sim$215 K) so this physical change should be assigned as a liquid–liquid transition[2]. In previous investigations[3], the lower liquid–liquid transition for the PHMs under consideration, T_{ll}, was detected at $\sim$260 K. The transition that resulted in the existence of two apparent activation energies investigated and discussed in this work showed

0032-3861/92/040883-03

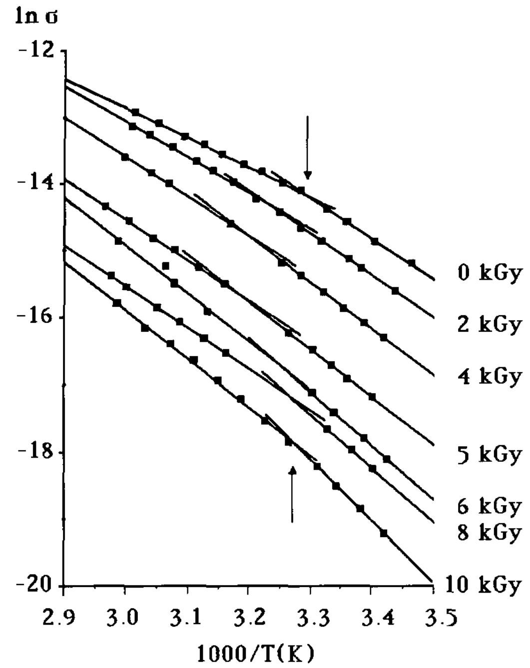

Figure 1 Arrhenius type plot of the d.c. conductivity at the selected doses for PHM resin with 76% maleate and 50% styrene. The $T_{l\rho}$ temperature range is indicated

Table 1 Dependence of the vitrification dose on the maleate to fumarate ratio in the PHM[a]

Maleate/ fumarate	Styrene (%)	D_1 (kGy)	$\bar{D}_1$ (kGy)	D_2 (kGy)	$\bar{D}_2$ (kGy)
1:1	30	3	3	3	3
	50	3		3	
3:1	20	4	4.5	4	4.5
	30	5		5	
	40	5		4	
	50	4		5	
10:1	30	4	4.5	4	5
	50	5		6	

[a] D_1, vitrification dose determined from the changes in the apparent activation energy with dose for temperatures below the $T_{l\rho}$ transition ($\bar{D}_1$ is the mean value). D_2, vitrification dose determined from the changes in the apparent activation energy with dose for temperatures above the $T_{l\rho}$ transition ($\bar{D}_2$ is the mean value)

no dependence on irradiation dose or styrene concentration and was assigned $T_{l\rho}$, the upper liquid–liquid transition.

When the polyester resin with styrene is exposed to the ionizing radiation, the crosslinking reaction starts. By interrupting the irradiation, the reaction stops. The temperature dependence of the d.c. conductivity was measured after each irradiation step so the changes in apparent activation energy could be monitored throughout the course of the reaction. As the reaction proceeded, the absolute value of the d.c. conductivity was lowered and its apparent activation energies both above and below $T_{l\rho}$ increased.

The values of the apparent activation energies in the temperature range above and below the liquid–liquid transition were plotted *versus* dose (*Figure 2*).

In the case of irradiation of PHM resin without styrene no change in the apparent activation energies with increase in dose was detected (*Figure 3*).

DISCUSSION

The change in the apparent activation energies of the d.c. conductivity of PHM resins in the temperature range under consideration could be caused by the change in the degree of ordering of polymer melt. Above the glass transition the polymer melt may still possess a certain low degree of short range local ordering and it does not behave as a true liquid. This ordering is based on

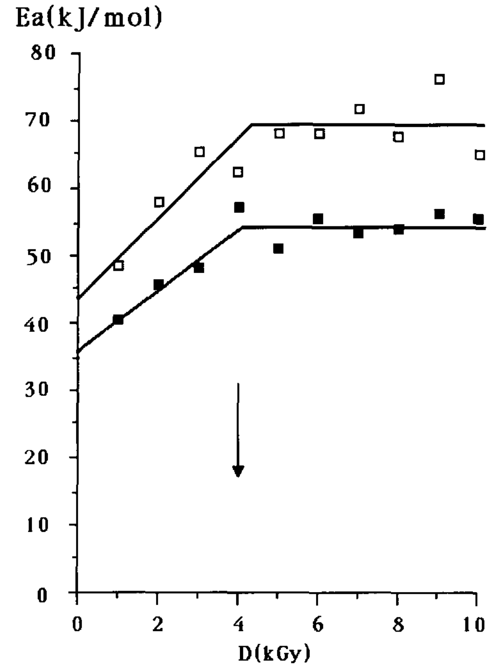

Figure 2 Dependence of the apparent activation energies of d.c. conductivity for PHM with 90% maleate and 30% styrene on radiation dose: apparent activation energies in the temperature range above (■) and below (□) the transition. An arrow indicates the vitrification dose at 4 kGy

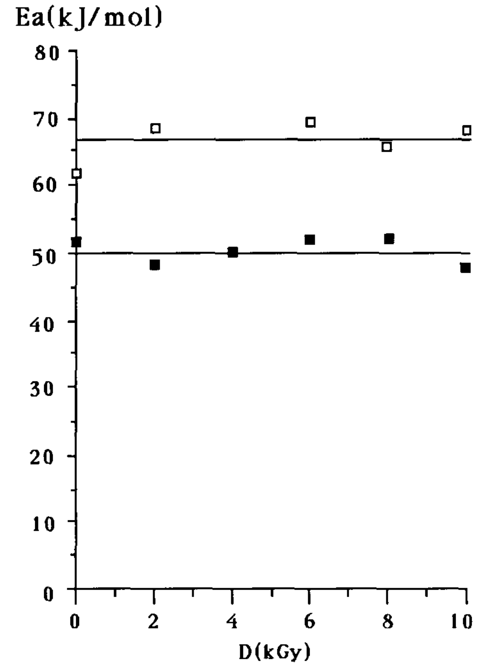

Figure 3 Dependence of the apparent activation energies of d.c. conductivity for PHM with 76% maleate without styrene on radiation dose. The apparent activation energies remained constant because there was no crosslinking. Symbols as in *Figure 2*

numerous Van der Waals and hydrogen bond interactions along the coiled polymer chain. These interactions can be of inter- and intramolecular type. In the temperature range of T_{ll}, intermolecular interactions break. The penetration of solvents and monomers into the coil is difficult so the dilution and crosslinking reactions are predominantly intermolecular processes. Therefore, by increasing the concentration of the solvent or the degree of crosslinking, T_{ll} becomes weaker and finally disappears. The upper liquid–liquid transition, $T_{l\rho}$, is the temperature range where the intramolecular interactions are broken and the polymer melt becomes true liquid. Because of the lack of solvents or monomers inside the coil, $T_{l\rho}$ should not be affected by dilution or crosslinking as is observed experimentally.

The styrene monomer addition to the PHM resins caused the viscosity drop that was followed by the drop in the apparent activation energies of d.c. conductivity compared to the undissolved sample. There was no significant penetration of the monomer into the polyester coil because styrene is a poor solvent for unsaturated polyester resins so its concentration had no influence on the $T_{l\rho}$ transition. The different maleate to fumarate ratios in the PHM resins studied also had no effect on the temperature range of the $T_{l\rho}$ transition.

Taking into account our previous results[3,4], which proved that hydrogen bonds were broken at T_{ll}, it can be concluded that in the unsaturated polyester resin $T_{l\rho}$ is caused predominantly by intramolecular hydrogen bond cleavage inside the polyester coil. It results in charge carrier generation and the increase in their mobility. These processes lower the apparent activation energy of d.c. conductivity in the temperature range above the $T_{l\rho}$ transition compared to the temperature range below it.

In the case of irradiation of the PHM resin with styrene, the ionizing radiation initiated the crosslinking reaction. The crosslinking reaction is predominantly intermolecular because of the lack of styrene inside the polyester coil that prevents intramolecular crosslinking. This explains why the two apparent activation energies caused by the $T_{l\rho}$ transition could be detected even at 10 kGy where the crosslinking of the polyester resin is completed. The temperature range of the $T_{l\rho}$ did not show any significant change with the degree of crosslinking (*Figure 1*).

The formation of the three-dimensional network lowered the mobility of the current carriers. The absolute current values became lower and both the apparent activation energies of d.c. conductivity became higher. The difference between lower and upper apparent activation energies remained approximately constant. In the temperature range of the measurements the apparent activation energy lowers only due to the $T_{l\rho}$ transition. At much higher doses it can be expected that the degradation brought in by ionizing radiation should lower the apparent activation energies, but in the dose range covered by these experiments degradation has no significant effect.

The increase in the apparent activation energies of the d.c. conductivity was not steady throughout the course of the crosslinking reaction. It reached a plateau at the dose that can be assigned to the vitrification of the system (*Figure 2*). In the PHM resins studied, the vitrification doses were between 3 kGy and 5 kGy. There is a correlation between the dose at which the plateau in the apparent activation energy increase during crosslinking is reached and the chemical structure of the resin. The greater the maleate content, the less reactive the polyester resin. The vitrification dose changed from ~3 kGy in the case of PHM with 51% maleate to ~5 kGy in the case of PHM with 90% maleate (*Table 1*). Thus, the vitrification dose increased with increase in the maleate to fumarate ratio in PHMs, i.e. as the crosslinking reactivity of the resin decreased.

The styrene content had no significant effect on the vitrification dose. In the case of irradiation of PHM resin without styrene, where no crosslinking reaction occurred, no change with increase in dose was detected in the temperature range of the $T_{l\rho}$ transition or in the apparent activation energy of d.c. conductivity (*Figure 3*).

CONCLUSIONS

Two different apparent activation energies of the d.c. electrical conductivity of PHM resins, in the range between 290 K and 350 K increased with the degree of crosslinking of resin and reached a constant value at a certain dose where vitrification of the system occurred. The vitrification dose depends on the maleate to fumarate ratio which determines the crosslinking reactivity of the resin, and does not depend on the styrene content in the concentration range (20–50%), investigated.

The existence of $T_{l\rho}$ and its temperature range were not affected by styrene addition or radiation crosslinking. This confirms the assumption that intramolecular short range local ordering based on hydrogen bonding disintegrated at that temperature. No dependence of the temperature of $T_{l\rho}$ on the maleate to fumarate ratio in PHM could be detected which is also consistent with its nature. Further investigations on the liquid–liquid transitions are in progress.

ACKNOWLEDGEMENT

The financial support by the Ministry for Science, Technology & Informatics of the Republic Croatia and by International Atomic Energy Agency Vienna under research contract no. 6128/RB is gratefully acknowledged.

REFERENCES

1 Owen, J. 'Comprehensive Polymer Science', Vol. II, Pergamon Press, Oxford, 1989, p. 669
2 Boyer, R. F. 'Polymer Yearbook 2' (Ed. R. A. Pethrick), Harwood Academic, Chur, 1985, p. 233
3 Jelčić, Ž., Ranogajec, F. and Pucić Miličić, I. *IEEE Trans. Electr. Insul.* 1985, **EI-20**, 459
4 Jelčić, Ž., Pucić Miličić, I. and Ranogajec, F. 'Proceedings of the 6th Tihany Symposium', Akademiai Kiado, Budapest, 1987, p. 511