



On the crystalline-amorphous supermolecular structure of poly(4-methyl-1-pentene) films cast from solution: experimental evidences and theoretical remarks.

A.Danch* and A.Gadomski⁺

*Silesian University, Institute of Physics, Uniwersytecka 4, 40-007 Katowice, Poland.

+Technical University of Bydgoszcz, Inst. of Mathematics and Physics, Dept. of Theoretical Physics, Al.Kaliskiego 7/402, PL-85796, Poland.

We regard the formation of crystalline-amorphous structure of polymeric films cast from solution. We pay a special attention to its formation on a level of single quasicrystalline domain, and try to embark on the problem, when a possibly large group of such domains has to be considered. In the former, one is nearly enforced to make use of a modification of the stochastic diffusion-limited aggregation model, first introduced by Witten and Sander. In the latter, certain diffusion-type (Potts-like) models, invented for polycrystalline microstructure formation, could be adopted. When considering the problem on the first level mentioned, one may notice an apparent agreement between experiment and theory, whereas on the second level, some conceptual similarity seems to be attractive.

© 2000 Elsevier Science B.V. All rights reserved.

1. INTRODUCTION

Some theoretical considerations have led to the conclusion that a crystal-amorphous interphase may exist in semicrystalline polymers, which would allow for the dissipation of the order existing at the crystal surface [1-4]. The role of the interphase as a transition region, where chains assumed their isotropic orientation different from those of a truly amorphous phase unperturbed by a presence of crystal domains, has been already discussed in 1962 [1]. The formation of the interphase is caused by steric packing problems. The main consequence of such a physical situation is that the thermodynamic properties of the chains located in the interphase differ when compared with bulk (unperturbed) amorphous state, i.e. due to some restriction in macromolecule fluidity. Therefore, in a semicrystalline polymer the glass transition could be extended towards higher temperatures. It might result in a T_g -distribution or an existence of two well-separated T_g 's, depending on how pronounced the interaction between the crystalline and the amorphous phases can be. To examine the molecular mobility of the interphase region one can use dielectric or mechanical relaxation spectroscopies. For these techniques the aspect of the extended glass transition is reflected as broadening of adequate peaks in recorded spectra [5].

Our previous study concerning poly(4-methyl-1-pentene) (PMP) provided the information about the temperature-dependent relaxation of interphase chains. Using dielectric and mechanical spectroscopies we were able to show that the rigid (perturbed by the presence of crystalline domains) amorphous phase relaxes much above T_g (glass transition) but below T_m (melting point). Also, a Differential Scanning Calorimetry (DSC) study showed T_g -distribution but in some cases two well-separated glass transitions were observed, giving evidences for the existence of the crystal-amorphous interphase [6-7]. Although the amorphous phases of different structure and the crystalline phase were found in PMP membranes, the problem of relationship between them remains unaddressed. It is well known that this observation and other factors like a size, a shape and a distribution of polymer aggregates in an amorphous matrix have strong influence on properties of polymeric materials. Five different modifications (designated I, II, III, IV, V) of isotactic PMP have been reported and the lattice constants of each of them have been presented [8-9]. An annealing process performed at different temperatures showed that for more perfect crystals the greater number of defects (holes) were found at or near the crystal edge. For the smaller crystals, defects could be found in the interior as well [10]. Therefore, it seems to be acceptable that the morphology of PMP can be described as consisting of lamellar crystals and an amorphous matrix. However, it is worth noticing that the differences exhibited by PMP films in previous experiments not only resulted from the degree of crystallinity or the type of unit cell but the lamellar crystal specific distribution, too [11-13,6-7].

In this work we present the structure model of opaque and transparent films obtained by casting on glass or teflon plates from the solutions of PMP in different solvents. The problem of crystal distribution in the amorphous matrix is discussed with particular attention to the conditions of aggregation. The preparation of the opaque films from the PMP solution in other solvents than cyclohexane and such large aggregates (diameter about 15mm) have not been reported till now.

When dealing theoretically with the structure formation problem in a reasonable way, one has to make use of necessary simplifications. First, it is convenient to assume that we work within the regime of diluted or at most semidiluted solution. It draws more or less automatically our attention to the problem of interactions in the system. Thus, it implies that our next simplification would be: neglect the long-range interactions among the solute molecules (polymer chains) and presume the (short-range) interactions among the solvent as well as solute molecules to be repulsive. Moreover, let us take the particle (solute molecule)-cluster (quasicrystal) interaction as being of van der Waals nature, but with its attractive part being seemingly pronounced. Let us make the same for the cluster-cluster aggregation process but assume that the attractive part takes only slightly favour, when comparing with the repulsive one (just to ensure that the cluster-cluster aggregation process is possible to occur). Let us finally neglect the interaction of the solution with the plate on which it is poured out. If the above drawn physical picture is accepted, one is able to state that the problem in question can be modelled both on a level of single quasicrystalline domain as well as on a level of groups of such domains.

2. EXPERIMENTAL

PMP is the same as used in previous work [6-7,11]. The films were obtained by casting on glass or teflon plates from solutions of 4% (as well 2, 1, 0.5 by weight %) PMP in several solvents, i.e. cyclohexane, carbon tetrachloride, benzene, etc. For all of them, except carbon tetrachloride, the solutions were obtained by dissolving the PMP pellets at the boiling temperature (T_b) of each solvent used within time sufficient to give dissolution. All such prepared films, except the benzene films, were free of residual solvent after several days of drying. The preparation procedure was described in more details elsewhere [6,11,13]. For additional important details, see captions of pictures in the next section.

In order to emphasise the shape of the aggregates observed in each step of the film formation process the pictures taken by a photo-camera were digitally processed (contrast, brightness and sharpness, etc.).

3. RESULTS AND DISCUSSION

As was shown earlier, the properties of the PMP films depend on a degree of crystallinity and on a distribution of crystallites in an amorphous matrix [6-7,12]. But size and shape of different crystalline forms observed in the films seem to be important too, especially, for the creation of opaque or transparent structures. The structure, which is built by chains being immersed in crystalline and/or amorphous domains, appears to be very sensitive to the conditions of the solution preparation and the films casting. X-ray studies showed that the possibility of formation of the different films (opaque or transparent) from the same solution, e.g. cyclohexane, was the consequence of lamellae packing in an aggregate and a diverse arrangement of aggregates in an amorphous matrix [14]. Also, an amorphous shell around the lamella, which seems to be responsible for an order or random lamellae packing in the aggregate, played important role in supermolecular structure creation. The conditions of the structure creation can be described in two groups. The first includes the solvent preparation parameters, the second, in turn, is connected with the casting and the formation of films. However, the temperature plays a dominant role in the both groups. It was possible under proper conditions to create the required supermolecular structure that gave the opaque or transparent film [13]. The scheme of the film formation for the PMP solutions prepared at the boiling temperature of the solvent could be described in three steps, as illustrated in **Figure 1**.

As was said above, the temperature is very important, especially, for the lamellar crystal growth. Under certain conditions the crystals formed of different perfection are square and nearly flat. They are larger but the number of them is smaller when the solution is prepared at low temperature (+20°C) [10]. If the temperature is high enough (the boiling temperature of the solvent), the second parameter, i.e. the time of stirring, influences their size and perfection. For the shorter time of stirring the films are opaque and the higher degree of crystallinity was pointed out from DSC endotherms. On the contrary the percent of crystallinity drastically decrease with increasing of stirring time. Therefore, on the basis of the experimental evidences, the first step of the film formation (see **Figure 1**) should be modified for the other solvent than cyclohexane, i.e. carbon tetrachloride, in order to take into consideration the time dependency in the model.

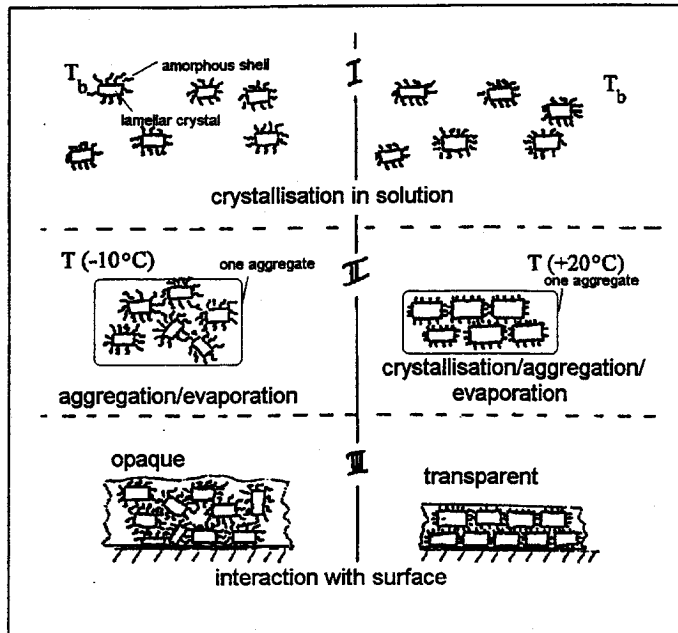


Figure 1. The three steps of the formation process for the cyclohexane PMP films: I- crystallisation in solution at the boiling temperature of the solvent; II- aggregation of lamellar crystals and evaporation of the solvent (further crystallisation in the case of the film formation at 20°C-right side); III- arrangement of the aggregates during further evaporation of the residual solvent and final creation of the supermolecular structure due to interaction with a plate.

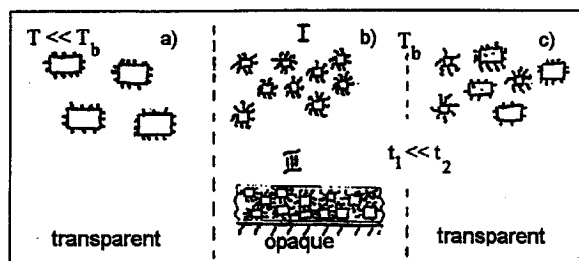
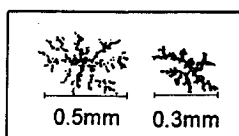


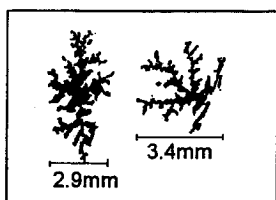
Figure 2. The scheme of the first step of the film formation (the crystallisation in solution): a) dissolving at temperature lower than T_b ; b) dissolving at T_b during short time (t_1); c) dissolving at T_b during long time (t_2). In the case of (a) and (c) the lamellar crystals are larger with smaller amorphous shell (the formed film is transparent), while in the case (b) the crystals are smaller with bigger amorphous shell and their number is higher (the films is opaque).

The modification of the first step with the three possibilities of the creation of the lamellar crystals, depending on time of dissolution and temperature, are given in **Figure 2**.

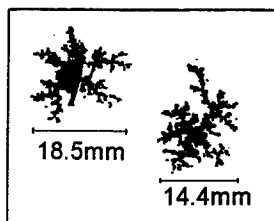
It has already been shown that in the PMP films cast from solution the single crystal is square and nearly flat with some defects (holes). The sizes and their perfection are very sensitive to the solvent and thermal treatment of the solution. The aggregation of those single crystals led to the formation of different forms of dendrites (fractals). With regard to the formation conditions, it was possible to take pictures of the PMP aggregates during the growth process in benzene. In other solvents the process was either too fast or occurred at very low temperature (-10°C). However, in the case of all opaque films, the aggregates resembled one another, showing only a little difference in their size and number. The PMP aggregates observed in a different step of film formation process (the 2% PMP solution in benzene) are presented in **Figure 3**. The real dimensions are given in the pictures. A drastic annealing and evaporation of the solvent could interrupt the process of the structure creation. Unfortunately, such a thermal treatment made the sample useless to further, i.e. dielectric or mechanical, investigation [6,7].



a) A first symptom of aggregation was observed after two weeks in a different part of the sample as points of its whitening. The number of aggregates was rather small and they had no contact one with another. The dimensions given in the picture show the real size of the aggregates. The sample was in a gel state.



b) After 24hs the aggregates were larger. The sample was still in a gel state. The number of aggregates insignificantly increased. Mostly, the aggregates observed earlier changed their size.



c) After next 48hs the size of the aggregates was rather large and they were visible in nearly whole sample. Now, the aggregation occurs also in third dimension, so the outlines of the aggregates were not so distinct. Due to the large aggregates overlapping, the sample was opaque in contrast to the transparent sample, where rather small aggregates built up the crystalline structure.

Figure 3. The PMP aggregates obtained in the II and III steps of the structure formation process. The solution was cast on a glass plate at room temperature. After two weeks the nucleation stage is observed, when the great amount of solvent had evaporated and the sample was in a gel state (a), first small aggregates were visible with naked eye. Next pictures were taken after 24 hours, showing a pure (mature) growth stage (b), and after 48 hours, showing three-dimensional growth stage (c).

In the case of PMP films cast from benzene solution, the structures looked like diffusion-limited aggregates (DLA) similar to those obtained in a computer experiment have been observed. A few examples of the aggregates are shown in Fig.3 and the comparison one of them with the DLA aggregate taken from the computer simulation is presented in Figure 4.

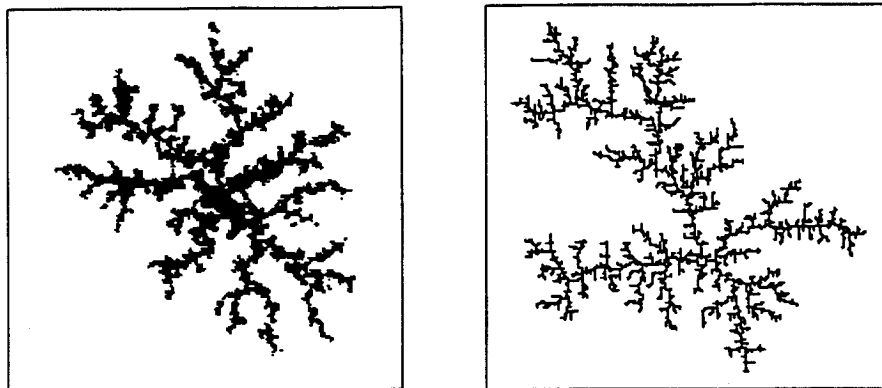


Figure 4. The aggregates observed in the solvent-cast films (left picture) and in the computer experiment performed in the frame of a simple stochastic model [15], which was a modification of Witten-Sander's model (right picture).

The morphology of the investigated samples, which was deduced from the earlier X-ray studies [14], consists of defected crystals distributed in a predominant amorphous phase. Moreover, the crystalline aggregates are preferentially oriented due to the interaction of the chains with the plate in the last stage of the film formation. The proposed model of the crystal aggregates shows that the crystal-amorphous interphase must exist in the PMP films that well explains the experimental results obtained by dielectric and mechanical spectroscopy and DSC measurements. It can be assumed that the aggregates formed by the lamellar crystals include interior "constrained amorphous" domains and "real amorphous" shell round them. One may conclude that not only the particular shape and large size of the dendrites cause the film being opaque but also the existence of two-component amorphous phase with well separated T_g values. Most likely, the solvent and the thermal treatment change the proportion between both amorphous phases. That would result in an order or random spatial arrangement of the aggregates.

In the introduction, it was mentioned that an attempt to modelling the membrane structure, even in a preliminary way, could be made effectively, when one considers it to be done on two levels. Namely, when considering the structure on the first (single quasicrystalline domain) level, a most suitable model to be chosen for describing the aggregation process is the Witten-Sander (diffusion-limited aggregation) computer model [16]. Since the amorphous phase in between plays a significant role and this fact cannot be easily omitted, just for assuring proper sticking conditions, the model should be slightly

modified. In consequence, we propose (see, figures) a modification of the condition for the sticking probability, P_{st} , which we propose to be of Arrhenius form [15]. For a given temperature T , the process of overcoming an energetic barrier by a macromolecule (E_{af}), that get eventually stuck to the growing quasi-crystal, is strongly related to the width of amorphous phase surrounding a single domain. So that the probability used in the simulations was

$$P_{st} = P_0 \exp(-E_{af}/RT), \quad (1)$$

instead of $P_{st} = 1$, which was applied in the original Witten-Sander model [15,16]. P_0 and R stand for constants. Because the width of the surrounding phase may change in course of time (t) (i.e., $E_{af} \equiv E_{af}(t)$), one can conclude that the problem may be roughly equivalent to prescribing a time-dependent condition on the corresponding interface. This observation appears to be of use for working with the problem analytically (cf. [17], for going into details), that means, when a very traditional Mullins-Sekerka quasi-static description is applied, with

$$\Delta c(r) = 0, \quad (2)$$

where $c(r)$ is a position dependent concentration field of Brownian particles (macromolecules), and with suitable boundary conditions. The internal boundary condition is a key point here [17], since it must be modified by including time t as a parameter (see, the reasoning presented above with $E_{af}(t)$ and look into [17] for details). When working with the problem on the level of ensemble(s) of domains, in turn, one would propose a cluster-cluster aggregation model [18], improved very much for colloidal environments. In the computer implementation the rules are very similar as in the (generic) Witten-Sander model, but the aggregation process does not take place on a single nucleus, but on a good number of mobile nuclei, rather. The process was studied much both in diffusion-limited as well as in chemical reaction limited regimes (see, [19] for an overview). When dealing with the problem in a diffusion-limited regime and in the late-times zone, it can, by using some analogy with Potts-like systems [20], be analytically described as a diffusion process in inhomogeneous medium [20],

$$\frac{\partial}{\partial t} f(x,t) = \frac{\partial}{\partial x} D(x,t) \frac{\partial}{\partial x} f(x,t) \quad (3)$$

with the diffusion function

$$D(x,t) = D_c x^\alpha t^\beta, \quad t \gg 1 \quad (4)$$

being time dependent, and including some information about crystalline-amorphous character of the medium. (Here, D_c is a constant, α contains some information about dimensionality (also, fractality) of the space, whereas β about the degree of crystallinity of the material as well as the adsorption of macromolecules; x represents the size of the single quasi-crystalline domain, and $f(x,t)$ is a distribution of domain sizes taken at time t , $f(x,t)dx$ is the number of

clusters of the size belonging to $[x, x+dx]$; cf. [21,17,20].). Both types of the modelling proposed result mostly in a final and very natural (asymptotic) result, namely [17,21]

$$R \propto t^\gamma, \quad (5)$$

i.e. that the (averaged) radius of a crystalline domain, R , taken either as a singular object or as "an averaged" object in an ensemble of domains (clusters) scales powerfully with the exponent γ . The exponent is quite rarely equal to $1/2$ (the case of the diffusion exponent) but exhibits a tendency to approach 1 (the mass convection exponent). Very small values, distinctly less than $1/2$, are also plausible; cf. [17,20]. The exponent γ carries an essential information about sticking conditions as well as crystallinity (or, amorphous nature) of the complex system in question; cf. [21] for details. In other words, it allows for offering in an analytical way, a consistent picture of explaining of the evolutions for the problem that was studied on the both levels mentioned (cf. Fig.2). It also provides a good rationale for using computer models (Witten-Sander or diffusion-limited cluster-cluster aggregation [18]) as a very essential supporting tool.

4. CONCLUDING REMARKS

As to the theoretical considerations briefly presented in this work, two types of remarks can be mentioned. A first type is said to be constructive (or even, optimistic) in the sense that it throws away all the possible doubts concerning the controlling factor(s) of the structure formation process. In our opinion (look again at the pictures presented), the studied process is controlled by diffusion because the domain possess dendritic character, no matter, whether we do investigate it on the single cluster or on the many clusters level of description. To our understanding of great importance can be the fact: whether the process is realised in a vigorous, i.e. superdiffusive way or is just slow down (subdiffusion). Because of a large number of physical factors influencing the process, one might risk a statement that quite rarely the aggregation or crystallisation will proceed in a normal diffusional regime. A second possible type of remarks can be called destructive (or, pesimistic). It is so because we are not only aware of simplifications but also of a pretty large number of "physical agents", that we left unconsidered. These are, e.g. the evaporation rate of solvent molecules during the structure formation process (drying), some neglect of the chemical nature of the solvent and solute molecules, lack of attempting on a possible account of impurities and kinetic obstacles for the behaviour of the system, etc.

The dominant role in the aggregation process plays the thermal treatment of the sample both in the step of dissolution when the lamellar crystals are created and in the step of polymer film formation, when the main aggregation takes place. One may conclude that not only the particular shape and large size of the aggregates cause the film being opaque but also the existence of two-component amorphous phase. Most likely, the physical agents mentioned above change the proportion between both amorphous phases. That would result in an order or random spatial arrangement of the aggregates. Finally note that because of existence of the time-temperature (t - T) equivalence principle in polymeric systems, time evolutions as well as temperature changes can be quite rigorously related to one another.

REFERENCES

1. P.J. Flory, *J. Am. Chem. Soc.*, **84** (1962) 2857.
2. P.J. Flory, D.Y. Yoon and K.A. Dill, *Macromolecules*, **17** (1984) 862.
3. D.Y. Yoon and P.J. Flory, *Macromolecules*, **17** (1984) 868.
4. S.K. Kumar and D.Y. Yoon, *Macromolecules*, **22** (1989) 4098.
5. L.C.E. Struik, *Physical Aging of Amorphous Polymer and Other Materials*, Elsevier, Amsterdam, 1978.
6. A. Danch and K. Jarzabek, in *Proceedings of the Third International Symposium on Far-From-Equilibrium Dynamics of Chemical Systems*, edited by J. Górecki, A.S. Cukrowski, A.L. Kawczyński, B. Nowakowski, World Scientific, Singapore 1994, pp350-359.
7. A. Danch, *J. Thermal Anal.*, **54** (1998) 151.
8. G. Charlet, G. Delmas, J.F. Revol and R.St.J. Manley, *Polymer*, **25** (1984) 1613.
9. G. Charlet, and G. Delmas, *Polymer*, **25** (1984) 1619.
10. D.R. Morrow, G.C. Richardson, L. Kleinman and A.E. Woodward, *J. Polymer Sci.*, **A2(5)** (1967) 493.
11. A. Danch and A. Gadomski, *J. Thermal Anal.*, **45** (1995) 1175.
12. A. Danch, A. Gadomski and D. Sęk, *Polish J. Environ. Studies*, **6** (1997) 5.
13. A. Danch, PhD thesis, Silesian Univ., Katowice, 1998.
14. A. Danch, M. Karolus and A. Burian- Proc. of SPIE, accepted.
15. A. Gadomski and Z.J. Grzywna, in *Proceedings of the Second International Symposium on Far-From-Equilibrium Dynamics of Chemical Systems*, Swidno (Poland), September 3-7, 1990, edited by J. Popielawski and J. Gorecki (World Scientific, Singapore, 1991), pp. 416-427.
16. T.A. Witten and L.M. Sander, *Phys. Rev. Lett.*, **47** (1981) 1400; for a specific but interesting realisation look also at M. Wolf, *J. Phys. A* **21** (1988) L159.
17. A. Gadomski, *Vacuum*, **50** (1998) 79.
18. A. Skjeltorp and P. Meakin, *Adv. Phys.*, **42** (1993) 1; A. Miller, K. Knoll and H. Mohwald, *Phys. Rev. Lett.*, **56** (1986) 2633.
19. J. Luczka, P. Hanggi and A. Gadomski, *Phys. Rev. E* **51** (1995) 5762; J. Luczka and R. Rudnicki, *Fractals*, **4** (1996) 543.
20. M. Niemiec, A. Gadomski, J. Luczka and L. Schimansky-Geier, *Physica A* **248** (1998) 365; J.C. Earnshaw and D.J. Robinson, *Phys. Rev. Lett.*, **72** (1994) 3682.
21. A. Gadomski, *Chem. Phys. Lett.*, **258** (1996) 6; *Ber. Bunsengesell. Phys. Chem.*, **100** (1996) 134; *Eur. Phys. J B*-in press (1999).