Microphase separation in athermal polymer solutions in 2D

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It is generally believed that in athermal conditions, which correspond to a situation in a good solvent, polymers are soluble in low molecular weight solvents at all concentrations. It such conditions, when interactions P-S P-P and S-S (where P stands for a polymer unit and S for a solvent) are equal there is no energetical contribution ΔH to the free energy of mixing $\Delta G = \Delta H - T\Delta S$ so the system should be miscible at all concentrations due to an increase in entropy. This approach does not take explicitly into account the excluded volume interactions. They can be taken into account by assuming suitable potentials thus giving a contribution to ΔG. Calculations based on Edwards hamiltonian were performed by Cosmas and Vlahos [1] for chains of different length. These authors concluded that there should be a miscibility gap, especially in 2D systems, the more pronounced the bigger is the difference in chain length. This conclusion was however not supported by other results. In the present work we report the results of MC simulations of longer chains in a full concentration range We used cooperative motion algorithm [2,3]. It allows simulation of dense systems (at full occupancy), including polymer melts, and is very efficient, which makes possible simulations for big chain length in reasonable time. The simulations were carried out in athermal conditions on a triangular lattice with periodic boundary condition. We show that in the system in which solvent molecules are taken into account, for sufficiently long chains a microphase separation takes place in 2D polymer solutions, even in athermal conditions. This effect is related to the strong excluded volume interactions in 2D systems where the chains cannot cross each other and the solvent molecules cannot cross the chains.

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[2] T. Pakula, K. Jeszka, Macromolecules **32**, 6821-30 (1999).
[3] T. Pakula, S. Geyler Macromolecules **20**, 2909-14 (1987).