Macromol. Symp. **2003**, *198,* 11-17

Solubility Islands for Polymer Blends – A New Option to Homogenize Incompatible Polymers?

Attila R. Imre
KFKI Atomic Energy Research Institute, H-1525 Budapest, P.O. Box 49, Hungary
E-mail: imre@sunserv.kfki.hu

Summary: Experimental results of liquid-liquid phase equilibrium in a polydisperse blend of two polyalkylsiloxane are presented here. The UCST has an unusual pressure dependence: pressure induced miscibility at moderate pressures and pressure induced immiscibility at higher pressures, above a double critical point. The cloud point curve has two maxima in (concentration, temperature) as well as in (concentration, pressure) space. Approaching the double critical point, the high and low pressure branches of the cloud point curve merge and in a certain stage of this merging, they form a miscibility island located inside the two-phase region. Islands of this kind can give us a new tool to mix virtually immiscible blends.

Keywords: blends, compatibility, miscibility islands, polysiloxanes, UCST

Introduction

A couple of years ago an unusual kind of phase diagram of polystyrene/ acetone system was published by Rebelo and Van Hook[1] – a small island of miscibility located inside of the hour-glass shaped two-phase region. The existence of these kinds of islands in the (concentration, temperature) space have been predicted a few years earlier[2] and can be expected in other systems. [3-5] In this short paper we would like to report the existence of a similar miscibility island in the (concentration, pressure) space, without giving complete theoretical explanation.

Solubility Island

On Figure 1/a we can see the schematic representation of the liquid-liquid loci in weakly interacting binary homopolymer systems (solutions and blends) at constant pressure. The system is homogeneous in medium temperature range; liquid-liquid phase transition can be induced by cooling or by heating. In some cases the high or the low temperature branch is missing; it can be masked by freezing or degradation, or it might be simply out of our experimental range. The cloud-point curves have two critical points: UCST (Upper Critical Solution Temperature, being the uppermost part of the low -temperature branch) and LCST (Lower Critical Solution Temperature).

DOI: 10.1002/masy.200350802

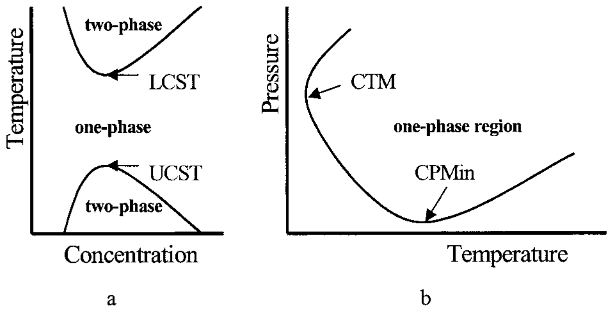

Figure 1.: a.: Schematic representation of the cloud-point curves in weakly interacting binary homopolymer solutions or blends. Critical points, UCST (Upper Critical Solution Temperature) and LCST (Lower Critical Solution Temperature) are marked by arrows. b.: Schematic pressure dependence of the critical liquid-liquid locus in weakly interacting homopolymer solutions and homopolymer blends. The two double-critical points, CTM (Critical Temperature Minimum) and CPMin (Critical Pressure Minimum) are marked by arrows.

In Figure 1/b we can see the schematic representation of the pressure dependence of the critical points[6,7]. The whole curve shown on Figure 1/b can be seen only in a few systems[6,7] ; in most cases only part of this curve can be observed. There are two extrema on this curve: one of them (CTM, Critical Temperature Minimum) can be seen for example in some solutions (like polystyrene/ methylcyclohexane solution[8]) as well as in a few binary blends[9] (like poly(ethylene glycol)/poly(propylene glycol) mixture[10]). The other one (CPMin) can be seen for example in polystyrene/acetone solution[1], but in most cases (like the polystyrene/methylcyclohexane solution[11]) this point is below p=0[12]. Both extrema can be seen for example in polystyrene/1,4-trans-dimethylcyclohexane solution[6] or in polystyrene/ methylcyclohexane/acetone ternary mixture[7].

Decreasing the pressure toward CPMin, the solubility gap between the UCST and LCST branches (in (concentration, temperature) space) is going to shrink and finally the branches touch each other at the UCST/LCST (forming a double critical point, CPMin)[9] and merge, forming a so-called „hourglass"-shaped phase diagram. In most systems, this CPMin can be seen only by decreasing the pressure below zero[6,7,12] ; i.e. by stretching the liquid. Stretched liquids are metastable [13,14] and the generation of negative pressure (high enough to reach the merging point of the UCST and LCST) is difficult, therefore this kind of double critical point can be seen rarely in experiments.

In some systems the cloud-point curve (in (concentration, temperature) space) might be double humped. By decreasing the pressure to approach a double critical point (CPMin) the

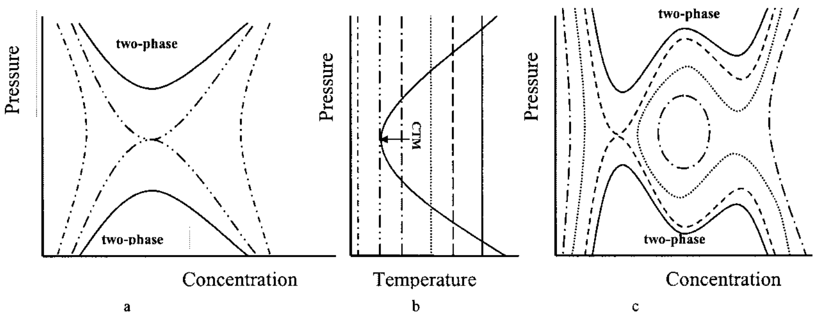

Figure 2.: Schematic representation of the liquid-liquid equilibrium in binary systems with a double critical point (CTM) on the UCST (b) and the merging of the low- and high-pressure branches with sinle (a) and double (c) maxima cloudpoint curves.

two branches will be joined first by the bigger humps, then by the smaller ones, creating first a peninsula, later an island of solubility. The double-humping of the cloud-point curve – which is crucial to get solubility island in weakly interacting binary polymer system – can be explained in two different ways: by the polydispersity of one or both components or by the strong concentration dependence of the Flory-Huggins type of interaction parameter.[1,3,15-20] This kind of solubility island has been found in polystyrene/acetone system[1].

Studying the system at constant temperature (instead of constant pressure) in the vicinity of CTM (Fig.2/b), we can see two cloud-point curves, one at higher pressures and the other one at lower pressures (Fig. 2/a, solid lines), similarly to the constant pressure case (Fig. 1/a). Approaching the CTM by decreasing the temperature, the two branches can merge and form an hourglass shaped phase diagram[8] (Fig. 2/a, dash-dotted lines). Although most theoretical works concerning the shape of the cloud-point curves in polydisperse systems have been done for p=constant case, we can expect that polydispersity causes similar effects (distortion or even double humping) on the cloud-point curve in the (concentration, pressure) space (fig. 2/c, solid lines). In this case, approaching the CTM by decreasing the temperature, we might get a solubility island (Fig.2/c, dash-dotted lines) - similar to the one found by Rebelo and Van Hook in polystyrene/acetone system in the vicinity of the CPMin[1] - but in this case it will be located around the CTM.

In a recent experiment a binary system of two polysiloxanes (already proved to have double humped cloud-point curve in (concentration, temperature) space in a blend of these two polymers with slightly different molecular weight[21]) has been studied by us. We have to emphasize here, that although the cloud-point curve is double humped, the coexistence curve has only a single maximum[9,21], i.e. we do not have three-phase equilibrium or three critical points on the UCST expected in case of double-humped coexistence curve.[18] Polydimethylsiloxane (PDMS, M_w= 1.74 kg/mol, M_w/M_n= 1.3) has been obtained from Wacker, polyhexylmethylsiloxane (PHMS, M_w=90.5 kg/mol, M_w/M_n=6.7) has been obtained from Hüls-Petrarch. Samples have been prepared by weight. Cloud-point temperatures have been measured in a stainless steel cell closed by two sapphyre windows[9,22] by measuring the intensity of the transmitted light with a photodiode, keeping the temperature at constant value and varying the pressure. The critical concentration (at atmospheric pressure) has been determined by the phase-volume ratio method and the obtained concentration was equal (within the experimental error) with the concentration corresponding to the local minimum on the cloud-point curve in the (concentration, temperature) space, as it has been expected in polydisperse systems.[15,23,24] Further details of the experiment is published elsewhere.[9]

Our experimental result obtained from the vicinity of the UCST (i.e. in the region of the local minimum) indicated that the cloud-point curve is double humped in the (concentration, pressure) space[9,21] as well as in the (concentration, temperature) one.

Having a double critical point on the UCST at accessible pressure (here it is around 50-60 MPa), 'separate' low pressure and high pressure cloud-point curves can be seen in (concentration, pressure) space at constant temperature (Fig.2). Without double humping these two curves would merge by forming an hourglass-shape (Fig.2/a). With double humping, first the two bigger humps would merge, then the two smaller ones, forming first a solubility peninsula then a solubility island (Fig.2/c, dotted and dash-dotted lines). Our experimental data focusing on the vicinity of the critical concentration (the local minimum of the lower and the local maximum of the upper curve on Figure 2/c) can be seen on Figure 3. The merging of the two branches and the forming of a solubility peninsula first (above 46 ^{0}C) and a solubility island later (around 44 ^{0}C) is clearly demonstrated, although the exact shape of the island needs further study. The island totally disappeared somewhere between 42 and 41 Celsius.

There are two crucial points which have to be fulfilled to get a solubility island in a weakly interacting binary polymeric system. One of them is the double humping of the cloud-point curves in the (concentration, pressure) space. Probably just like the similar phenomena (in (concentration, temperature) space), this phenomena is also caused by the polydispersity.

The other crucial point (to have a double critical point on the UCST branch) can be explained by a pressure-dependent excess volume of mixing.[22] According to some recent results, the existence of this point – i.e. the turning of dP/dT from negative to positive - is quite general[6,7,22,25-27], but for a lot of polymer blends the experimentally obtained pressure

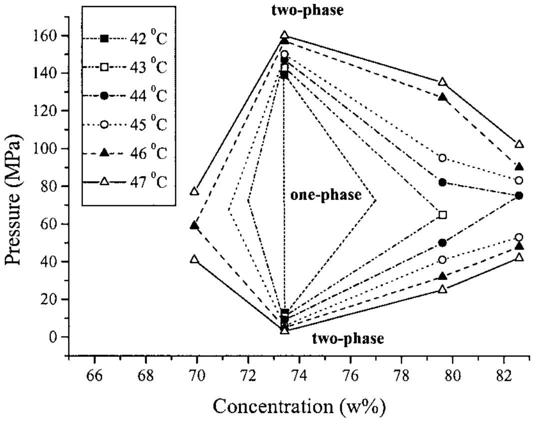

Figure 3.: The appearance of a solubility island in PDMS/PHMS blend. The connecting lines are only guides to the eye. Above 47 Celsius the high- and low-pressure branches are separated. Around 46 Celsius the two higher peaks merge (see Figure 2.), forming a solubility peninsula. At 44 Celsius the lower peaks merge too, forming an island of solubility which disappears between 42 and 41 Celsius.

dependence of the UCST seems to be monotonous[28-30], i.e. the double critical point is usually located in the experimentally not so easily accessible P<0 region.[22]

Solubility islands and compatibilization

The importance of this solubility island is twofold. First, it is theoretically important to show that the system behaves similarly around different kinds of double critical points[6,7] (the one around CPMin) – see the referred polystyrene/acetone system[1] -, and the other one around CTM). The second importance is a practical one. In most cases ’immiscible’ refers that the binary system exhibits hourglass shaped cloud-point curves in (concentration, temperature) and/or (concentration, pressure) spaces. In these cases homogeneous system can be prepared only with small amount of component A + big amount of component B (for example 0.1% A+99.9% B) and vice versa, but the two components cannot be homogenized at “medium” concentrations. The existence of a solubility island located inside of the hourglass region shows us, that seemingly incompatible systems might have a small island of compatibility somewhere in the (concentration, pressure) space (Fig. 4). While the other kind of island (in (concentration, temperature) space) is usually located at very high temperatures (over the degradation temperature) and mainly on negative pressures – at the merging of the UCST and

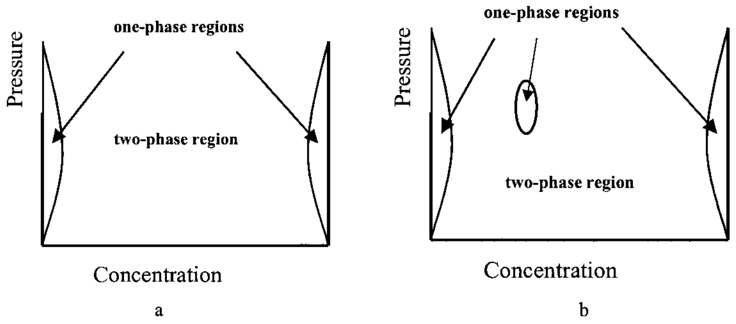

Figure 4.: Schematic representation of the cloud-point curves of two virtually immiscible polymer blends a.: without miscibility island, b.: with miscibility island.

LCST [12,31] -, this one – being in lower temperature - might give us a usable tool to homogenize some virtually incompatible systems.

Conclusions

In polymer blends (similarly to polymer solutions) an extremum (Critical Temperature Minimum) exists on the UCST, where pressure induced miscibility turns to pressure induced immiscibility . For most blends this extremum is located at negative pressure, but in the studied polyalkylsiloxane mixtures it is located on positive pressure; i.e. for these mixtures the UCST - as a function of pressure - is curved and exhibits an extremum. Due to this shape two separate branches can be seen on the concentration-pressure diagram (at constant temperature): a high pressure one and a low pressure one. Approaching the extremum on the UCST –by decreasing the temperature - these two pressure branches can merge, first by the bigger humps (forming a half hourglass-shaped cloud point curve with a miscibility peninsula) then by the smaller humps (forming the "usual" hourglass-shaped cloud point curve, but leaving a small miscibility island inside of the two-phase region). Further approaching the extremum this island shrinks and finally disappears, leaving hourglass-shaped cloud point curve, with two small one-phase parts (at very high and very low concentrations) and a big two-phase regime, located at medium concentrations.

Based on this result, two "virtually" incompatible polymer blends might have a small island of miscibility deep inside of the two-phase region. The existence of these islands might give us a novel way to homogenize virtually incompatible polymers.

Acknowledgement

The author thanks Prof. B.A. Wolf for his helpful suggestions and for providing the experimental setup for this measurement. This work was partially supported by the Hungarian Science Foundation (OTKA) under contract number F 034333. The author also thanks for the Humboldt Foundation for sponsoring his stay in Germany and for the members of the research group of Prof. Wolf (Johannes Gutenberg Univ., Mainz, Germany) – particularly T. Haase and P. Glöckner for the characterisation of the PDMS sample - for their help and hospitality. A.R.I. was also supported by the Bolyai Research Fellowship.

[1] Rebelo, L.P., Van Hook, W.A., *J. Polym. Sci. B.*, **1993**, *31*, 895
[2] Qian, C., Mumby, S.J. and Eichinger, B.E., *J. Polym. Sci. B*, **1991**, *29*, 635
[3] Rebelo, L.P.N., de Sousa, H.C. and Van Hook, W.A., *J. Polym. Sci. B.*, **1997**, *35*, 631
[4] de Sousa, H.C. and Rebelo, L.P.N., *J. Polym. Sci. B.*, **2000**, *38*, 632
[5] de Sousa, H.C. and Rebelo, L.P.N., *J. Chem. Thermodyn.*, **2000**, *32*, 355
[6] Imre, A.R., Melnichenko, G. and Van Hook, W.A., *Phys. Chem. Chem. Phys.*, **1999**, *1*, 4287
[7] Imre, A.R., Melnichenko, G. and Van Hook, W.A., *J. Polym. Sci. B*, **1999**, *37*, 2427
[8] Vanhee, S., Kiepen, F., Brinkmann, D., Borchard, W., Koningsveld, K. and Berghmans, H., *Macromol. Chem. Phys.*, **1994**, *195*, 759
[9] Imre A.R., Kraska, T. and Yelash, L., *Phys. Chem. Chem. Phys.*, **2002**, *4*, 992
[10] Steinhoff, B., Rüllmann, M., Kühne, L. and Alig, I., *J. Chem. Phys.*, **1997**, *107*, 5217
[11] Imre, A. and Van Hook, W.A., *J. Polym. Sci. B.*, **1996**, *34*, 751
[12] Imre, A. and Van Hook, W.A., *Chem.Soc.Rev.*, **1998**, *27*, 117
[13] Debenedetti, P.G., *Metastable Liquids: Concepts and Principles*, Princeton University Press, Princeton, NJ, **1996**
[14] Imre, A., Martinás, K., Rebelo, L.P.N., *J. Non-Equilib. Thermodyn.*, **1998**, *23*, 351
[15] Koningsveld, R., Onclin, M.H. and Kleintjens, L.A., in *Polymer compatibility and incompatibility, Principles and Practices*, MMI Press Symposium Series, vol.2, (Ed.: K. Solc), Harwood Academic Publisher, Chur, **1982**
[16] Kleintjens, L.A., Schoffeleers and H.M., Domingo, L., *B. Polym. J.*, **1976**, *8*, 29
[17] Koningsveld, R., and MacKnight, W.J., *Polym. Int.*, **1997**, *44*, 356
[18] Vanhee, S., Koningsveld, R., Berghmans, H. and Šolc, K. et al, *J. Polym. Sci. B.*, **1994**, *32*, 2307
[19] Šolc, K., Stockmayer, W.H., Lipson, G.E.J. and Koningsveld, in *Multiphase Macromolecular Systems*, B.M. Culberston, Ed., Plenum Press, New York, **1989**, vol. *6*, p.5
[20] Šolc, K., Kleintjens, L.A. and Koningsveld, R., *Macromolecules*, **1984**, *17*, 573
[21] Stammer, A., Wolf, B.A., *Polymer*, **1998**, *39*, 2065
[22] Imre, A.R., Melnichenko, G., Van Hook, W.A. and Wolf, B.A., *Phys. Chem. Chem. Phys.*, **2001**, *3*, 1063
[23] Tsuyumoto, M., Einaga, Y. and Fujita, H., *Polymer J.*, **1984**, *16*, 229
[24] Borchard, W., Frahn, S. and Fischer, V., *Makromol. Chem. Phys.*, **1994**, *195*, 3311
[25] Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M., *Polymer*, **1975**, *16*, 445
[26] Urbanowicz, P., Rzoska, S.J., Paluch, M., Sawicki, B., Szulc, A. and Ziolo, J., *Chem. Phys.*, **1995**, *201*, 575
[27] Economou, I.G., *Macromolecules*, **2000**, *33*, 4954
[28] Wolf, B.A., *Pure Appl. Chem.*, **1997**, *69*, 929
[29] Rabeony, M., Lohse, D.J., Garner, R.T., Han, S.J., Graessley, W.W. and Migler, K.B., *Macromolecules*, **1998**, *31*, 6513
[30] Kumar, S., *Macromolecules*, **2000**, *33*, 5285
[31] Imre, A., and Van Hook., W.A., *J. Phys. Chem. Ref. Data*, **1996**, *25*, 637 (Erratum: **1996**, *25*, 1277)