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# On the Compatibility of Polystyrene/Acrylonitrile-Butadiene-G-Styrene Copolymer/Solvent System

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## Summary

Influence of the temperature on the compatibility of the polystyrene / AB-g-S graft copolymer / cyclohexanone have been studied by light scattering and viscosity measurement. It was established that the compatibility of components is changed in the temperature range where the conformational transitions take place.

## Introduction

The study of the compatibility of polymer / polymer / solvent systems by viscosity and light scattering measurements in diluted solutions, has been subject of numerous reports (1 - 12). The results of the two methods and the utilization of extrapolated values permit to get information not only on the compatibility but also on the conformational transitions which takes place in the system depending on molecular weight, temperature, composition, etc.

Earlier studies (13 - 15) regarding multicomponent systems containing styrene polymers have made evident either the $\Theta$ temperature or a transition from the segregated conformation to a gaussian type one in the 34 - 50°C domain depending on the solvent or copolymer nature and composition.

The purpose of the present paper was to investigate the behaviour of polystyrene / graft copolymer AB-g-S /cyclohexanone systems by light scattering and viscosity measurements at 20 - 50°C.

## Experimental

Polystyrene (PS) with $\overline{M}_w = 3.5 \times 10^5$ and an AB-g-S graft copolymer with average composition : 5.7 % moles butadiene, 48.7 % moles styrene and 45.6 % moles acrylonitrile (as established by NMR measurements) and $[\eta]_{\text{toluene, } 25^\circ C} = 0.557$ dl/g were received from Borzegti Petrochemical Plant. Both products were initi-

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ally purified by extraction with a nonsolvent or by precipitation.

The mixture ratios of the components were: 90/10, 75/25, 50/50, 25/75 and 10/90. The solvent used was cyclohexanone freshly distilled.

The study of PS / AB-g-S / solvent system compatibility has been carried out by viscosity, light scattering and interferometrical measurement in diluted solutions.

As a preliminary, the insoluble part from AB-g-S copolymer was removed by centrifugation the solutions at 16,000 r/m, for 20 minutes followed by filtrating through a G-4 filter.

Then the concentration corrections were made either by weighing the insoluble part after being taken to a constant weight or by the evaporation of a known amount of the filtred solution.

The viscosity of the single components and that of the mixtures in the mentioned ratios, were measured in cyclohexanone diluted solution using a PCL suspended level dilution viscometer. A serie of six solutions were prepared over a range of concentration of 0.3 - 1 g/dl at 20, 25, 35, 40 and 50°C, within an accuracy of + 0.2°C. The same solutions were used in the light scattering and interferometrical measurements.

The light scattering determinations were made with a PCL - Peaker instrument using the following conditions : range of temperature 20 - 50°C, angular domain 40 - 90° and wave length 4360 Å. From the dependence $(c/R_\theta)_{\theta=0} = f(T)$ (where $R_\theta$ represents the intensity Rayleigh at the $\theta$ diffusion angle of the system, and c - concentration), the optical density modifications were observed.

The refractive index increments were determined by Zeiss interferometer at the same wave length and temperature range.

## Results and discussion

Compatibility estimation of the PS / AB-g-S system in the presence of cyclohexanone was firstly made by comparison of the values of limiting viscometric numbers, evaluated by extrapolation procedures (using the Huggins and Fuoss - Mead equations). From the slope line then were estimated the values $K_I$ and $K_{II}$.

From the $[\eta]$ versus composition plots presented in the figure 1, one can observe that the curves shape is highly dependent of the working temperature.

It can be seen that at 25 and 50°C the values for all the mixtures are greater than additive ones, while at 35 and 40°C, the experimental points are placed along a line traced as if any interaction between the components would be missing the behaviour being close to that of an ideal one.

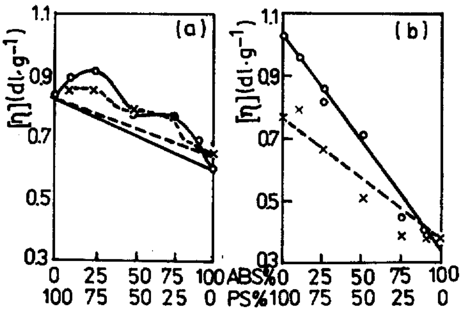

Figure 1. The variation of the [$\eta$] versus composition for PS / AB-g-S mixtures at different temperatures : (a) 25°C (o, ——) and 50°C (x, ---); (b) 35°C (x, ---) and 40°C (o, ——).

A more evident variation with temperature of the behaviour of these systems is shown in figure 2.

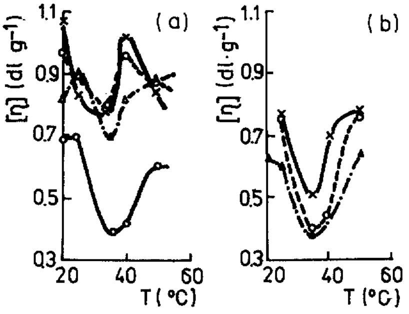

Figure 2. The variation of the [$\eta$] versus temperature for PS / AB-g-S systems at different mixture ratios : (a) PS (x); 90 % PS/10 % AB-g-S (•); 75 % PS/25 % AB-g-S (△); 10 % PS/90 % AB-g-S (o); (b) 50 % PS/50 % AB-g-S (x); 25 % PS/ 75 % AB-g-S (•); AB-g-S (△).

The variation with temperature is typical for each system, but all have a minimum of the viscosity in the range of temperature between 30 and 40°C.

Large deviations from the theoretical behaviour concerning dependence of [$\eta$] versus temperature is observed in the same range of temperature also in the

Table 1. $K_I$ and $K_{II}$ values for the PS/ABS/cyclohexanone mixtures at different temperatures

| Sample | 25°C | | 35°C | | 40°C | | 50°C | |
|---|---|---|---|---|---|---|---|---|
| | $K_I$ | $K_{II}$ | $K_I$ | $K_{II}$ | $K_I$ | $K_{II}$ | $K_I$ | $K_{II}$ |
| PS | 0.3178 | 0.1234 | 0.5862 | 0.0867 | 0.2522 | 0.1808 | 0.2739 | 0.1563 |
| 90 PS/10 ABS | 0.3158 | 0.1685 | 0.5911 | 0.0108 | 0.3147 | 0.1699 | 0.3398 | 0.1558 |
| 75 PS/25 ABS | 0.2185 | 0.2054 | 0.7885 | -0.2057 | 0.2690 | 0.1773 | 0.2306 | 0.2019 |
| 50 PS/50 ABS | 0.3567 | 0.1315 | 1.3260 | -0.3460 | 0.4503 | 0.0992 | 0.1978 | 0.2326 |
| 25 PS/75 ABS | 0.1709 | 0.2478 | 2.2430 | -0.9935 | 1.6021 | -0.6296 | 0.0843 | -0.3677 |
| 10 PS/90 ABS | 0.2730 | 0.2100 | 2.0770 | -1.1427 | 0.6188 | -0.6188 | 0.4162 | 0.1278 |
| ABS | 0.4687 | 0.0795 | 1.5475 | -0.7089 | | | 0.0828 | 0.2935 |

$K_I$ and $K_{II}$ values, presented in the table 1.

The sum $K_I$ and $K_{II}$ greatly differs from 0.5 at 35 and 40°C. The deviations increase with the increasing of the copolymer content.

These variations are typical for the systems which present conformational transitions at temperature modification (13 - 15).

To confirme this hypotesis we have done light scattering measurements following the variation of Rayleigh intensity with the diffusion angle and temperature.

For the polystyrene and the mixtures with a high content of polystyrene (75/25, 90/10), the curve extrapolation $c/R_\theta$ as a function of the diffusion angle at $\theta = 0°$ could be carried out without any difficulty at all working temperature; for the AB-g-S or the mixtures with high AB-g-S content (10/90; 25/75; 50/50) these extrapolations couldn't be carried out (figure 3) of course, the solvent quality and the nature of the two polymer components are responsable for the mentioneted difficulties.

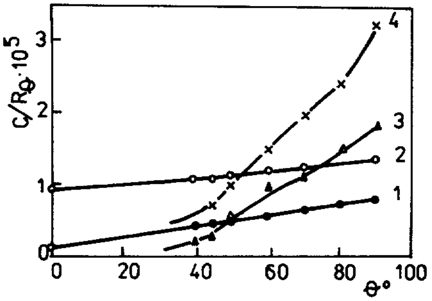

Figure 3. Dependence of Rayleigh's rapport against the diffusion angle : (1) - 90 % PS/ 10 % AB-g-S (26°C); (2) PS (25°C); (3) AB-g-S (32°C); (4) 50 % PS/50 % AB-g-S (24°C).

For the mixtures with a high content of PS the variation of $(c/R_\theta)_{\theta=0}$, a value proportional to the second virial coefficient, was followed as function of temperature (figure 4).

In the temperature range 30 - 40°C there was observed the apparition of some inflection the same as in the case of viscosity measurements. While the average molecular weight and mixture composition does not change with temperature, we suppose that the optical density variations are due to the refractive index increment change.

From the table 2 on can see a deviation from the linear increase of the refractive index increment with temperature over the temperature range 30 - 40°C. It is a proof what the temperature variations and solvent quality determine the appearance of the conformational transitions (16).

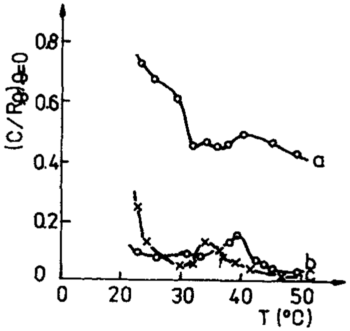

Figure 4. Variation of $(c/R_\theta)_{\theta=0}$ against the temperature for : (a) PS; (b) 90 % PS/10 % AB-g-S; (c) 75 % PS/25 % AB-g-S.

TABLE 2
The refractive index increments against the temperature

| T°C | PS | AB-g-S | PS / AB-g-S 25/75 | PS / AB-g-S 75/25 | PS / AB-g-S 50/50 |
|---|---|---|---|---|---|
| 20 | 0.1482 | 0.1016 | 0.0996 | 0.1330 | 0.1270 |
| 23 | 0.1500 | 0.1020 | 0.0997 | 0.1391 | 0.1275 |
| 25 | 0.1510 | 0.1023 | 0.1000 | 0.1415 | 0.1285 |
| 28 | 0.1511 | 0.1035 | 0.1041 | 0.1435 | 0.1288 |
| 30 | 0.1515 | 0.1026 | 0.1026 | 0.1444 | 0.1321 |
| 32 | 0.1522 | 0.1031 | 0.1022 | 0.1457 | 0.1315 |
| 34 | 0.1525 | 0.1044 | 0.1014 | 0.1578 | 0.1319 |
| 36 | 0.1544 | 0.1046 | 0.1016 | 0.1637 | 0.1348 |
| 38 | 0.1574 | 0.1046 | 0.1019 | 0.1695 | 0.1361 |
| 40 | - | 0.1046 | 0.1030 | 0.1730 | 0.1380 |
| 44 | - | 0.1046 | 0.1048 | 0.1766 | 0.1382 |
| 47 | - | 0.1035 | 0.1067 | 0.1817 | 0.1393 |

As we have outlined before the variation $(c/R_\theta)_{\theta=0}$ with temperature couldn't studied for the mixture with a high content of AB-g-S. Nevertheless, as on can observe in figure 5, for different scattering angles, the temperature variation of $c/R_\theta$ ratio presents the same anomalies in the mentioned temperature range.

Change of the styrene polymers conformation in different solvents, in the temperature range 30 - 40°C were made evident by other authors too (17 - 19).

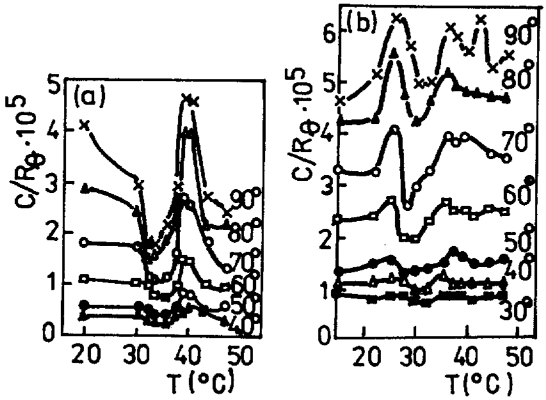

Figure 5. Variation of $c/R_\theta$ against the temperature : (a) AB-g-S;
(b) 25 % PS/75 % AB-g-S.

The changes observed are more marked because the cyclohexanone is a poor solvent for this system and, because of the tendency of the grafted copolymer to present molecular aggregation, micellation and non-gaussian distribution of segments.

In the case of polymer mixtures, the degree of components compatibility changes, at the same time with the conformational modification, since the number of like and unlike contacts is different.

The present results point out that non-similar heterocontacts decrease in the temperature range 35 - 40°C, where we can consider that θ temperature of the components and the mixtures exist.

A precise location of these temperature can't be achieved because one of the components is a auto-incompatible graft copolymer AB-g-S (20,21) which presents many θ temperatures, like the mixtures which contain it.

New arguments concerning the incompatibility of the two components of the PS/AB-g-S system will be presented in a next paper describing their behaviour in concentrated solutions and in solid state.

## References

1. CRAGG L.H. and BIGELOW C.C., J.Polym.Sci., B 2, 883 (1964).
2. ZELLINGER J. and HEIDINGSFELD V., Sbornii Vysoko. Chemiko-Technol. v Praze Org. Technol., C 9, 63, (1966).
3. KRIGBAUM W.R. and WALL F.T., J.Polym.Sci., 5, 505, (1950).
4. VASILE C. and SCHNEIDER I.A., Makromol.Chem., 141, 127 (1971).
5. KIRKWOOD J.R. and GOLDBERG R.J., J.Chem.Phys., 18, 54 (1950).
6. STOCKMAYER W.H., J.Chem.Phys., 18, 58 (1950).
7. CASASSA E.F. and EISENBERG H., Adv.Protein.Chem., 19, 287 (1964).
8. STOCKMAYER W.H. and STANLEY H.E., J.Chem.Phys., 18, 153 (1950).
9. HYDE A.J. and TANNER A.G., J.Colloid Interface Sci., 28, 179 (1968).
10. KRATOCHVIL P., VORLICEK J., STRAKOVA D. and TUZAR Z., J.Polym.Sci., 13, 232 (1975).
11. KUHN R. and CANTOW H.J., Makromol.Chem., 122, 65, (1969).
12. VAN DEN ESKER M.W.J. and VRIJ A., J.Polym.Sci., Phys.Ed., 14, 1967 (1976).
13. DONDOS A., J.Polym.Sci., Polym.Lett.Ed., 9, 871, (1971); Makromol.Chem., 135, 181 (1970).
14. DONDOS A., REMPP P. and BENOIT H.C., Polymer, 13, 97 (1972).
15. DONDOS A. and BENOIT H.C., C.R.Acad.Sci., (Paris), C, 271, 1055(1970).
16. HELLER W., J.Polym.Sci., Phys.Ed., 4, 209 (1966).
17. HAHN C.C., Polymer, 20, 1083 (1979).
18. ENYIEGBAUM M. and HOURSTON D.J., Polymer, 20, 817 (1979).
19. BAZUAYE A. and HUGLIN M.B., Polymer, 20, 44 (1979).
20. KRANZ D., MORBITZER L., OTTO K.H. and CASPER R., Angew.Macromol.Chem., 58/59, 213 (1977).
21. NOWMANN L.V. and WILLIAMS J.C., Polym.Eng.Sci., 18, 893 (1978).

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