

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Separation into Phases of Polymer Mixtures in Solution

O. Fuchs^a

^a Farbwerke Hoechst A.G., Vormals Meister Lucius & Brüning Frankfurt am Main, West Germany

To cite this Article Fuchs, O.(1971) 'Separation into Phases of Polymer Mixtures in Solution', Journal of Macromolecular Science, Part A, 5: 2, 469 – 486

To link to this Article: DOI: 10.1080/00222337108069393

URL: <http://dx.doi.org/10.1080/00222337108069393>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NEW INTERPRETATIONS

Separation into Phases of Polymer Mixtures in Solution

SUMMARY

When three different polymers are dissolved in a common solvent and the total polymer concentration is above a certain value, three liquid layers are obtained because of the limited compatibility of the polymer components with one another. Tests have been carried out at room temperature on solutions of polystyrene + polyvinyl acetate + polyvinyl chloride in tetrahydrofuran, and polystyrene + polyvinyl acetate + atactic polypropylene in benzene. Analysis of the individual layers yielded the following results: each polymer is always contained in each layer; the mixing ratios of the polymers in the three layers are generally different from one another and differ also from the mixing ratio of the starting mixture; each of the three layers is distinguished from the others by the fact that a specific polymer has been accumulated therein in preference to the other polymers. Concerning the quantitative distribution of the polymers among the layers, some laws could be found which can be explained qualitatively on the grounds of molecular-physical considerations. A solution of polystyrene + polyvinyl acetate + polyvinyl chloride + atactic polypropylene in tetrahydrofuran (equal amounts of polymers, total concentration about 10 g/100 ml) forms four layers, the composition of which was also determined by analysis.

When solutions of polymer mixtures are evaporated, separation into phases takes place because the polymers become incompatible with one another when the concentration exceeds a certain value. As a result, strongly inhomogeneous films are obtained after evaporation of the solvent. If the inhomogeneity of the films is not taken into consideration, misleading results may be obtained in the analysis of the films.

It is shown that in the system polystyrene + polyvinyl acetate, with tetrahydrofuran as solvent, surprising phenomena appear on the addition in stages of cyclohexane. The phenomena are due to the overlapping of separating and dissolving processes which have, in part, opposite actions.

1. PROBLEM

In an earlier article [1] we showed that two liquid phases are formed above a certain polymer concentration in a solution of polystyrene + polyvinyl acetate in a common solvent because of the limited compatibility* of the polymers, each phase containing both kinds of macromolecules. The mixing ratios of the two polymers in the phases differ from the mixing ratio of the total mixture. When, e.g., 2 g polystyrene and 2 g polyvinyl acetate are dissolved in 50 ml benzene, the lower layer formed by separation into phases contains about 30% more polyvinyl acetate than polystyrene while in the upper layer the amount of polystyrene is 2.7 times the amount of polyvinyl acetate. In the course of separation the polymers are partially distributed among the phases according to their molecular weights. It has also been shown that the separation processes depend on the mixing ratio of the two macromolecular components, their molecular weight, the nature of the solvent, and the total polymer concentration.

These results were the reason for expanding the research to more complicated systems and for studying some further effects connected with the partial compatibility of polymer mixtures.

The following were examined:

- a) Appearance and composition of a film obtained by evaporation of a solution of two polymers in a common solvent.
- b) Distribution of the individual polymer components among the layers formed when three or four different macromolecular substances are dissolved in a common solvent.
- c) Behavior of a solution of two polymers in a common solvent on dilution with a nonsolvent for one of the polymers.

2. SEPARATION PROCESSES DURING EVAPORATION OF A SOLUTION OF TWO POLYMERS

If a sufficiently small total concentration of the two dissolved polymers is chosen (e.g., below 2%), a homogeneous solution is generally obtained. When the solvent is gradually evaporated, turbidity appears (formation of

*The word "incompatibility," which is commonly used in the literature, is misleading and has deliberately been avoided because a certain compatibility always exists between different polymers.

microphases in the mixture) when the concentration exceeds a limit concentration c_{gr} of the compatibility. When the solution is further evaporated, the polymer concentration is increased in each microphase, whereby further separations into phases continuously take place in the individual microphases. Finally a film is obtained in which the polymer components are distributed very nonuniformly.

To examine the extent of the expected effects, the following evaporation tests were made: polystyrene + polyvinyl acetate in benzene, in tetrahydrofuran, and in ethyl acetate, respectively; polystyrene + polyvinyl chloride in tetrahydrofuran; polyvinyl acetate + polyvinyl chloride in tetrahydrofuran; and polyacrylonitrile + polyvinyl acetate in dimethylformamide. The solutions were evaporated at about 100°C in a stream of N_2 . The time of drying was generally about 15 hr. No solvent residues could be detected in the films by IR spectroscopy. Spotted and turbid films were obtained, which shows that the polymers are distributed in the films very nonuniformly.

As mentioned above, in the separation into phases of a solution of polystyrene + polyvinyl acetate, the polyvinyl acetate is accumulated in the lower layer because of the higher density of the solution (while the polystyrene is accumulated in the upper layer). To examine whether the composition of the polymer film is also influenced by this separating effect, the composition of the two surface zones of the film was determined by IR spectroscopy according to the reflection method. In each case a higher concentration of polyvinyl acetate was found in the lower zone than in the upper one. The values obtained varied within wide limits and were for various places of the surface zones within the range of 60 to 90% polyvinyl acetate in the lower zone and 80 to 95% polystyrene in the upper zone.

This result is of immediate practical importance: if only a cut-off portion of a film is used for analyzing inhomogeneous mixed polymer films obtained in the manner described above or in a different way, e.g., by kneading of polymer melts, different results are likely to be obtained for the individual portions of the film. We have studied this source of error for a film of polystyrene-polyvinyl acetate that had been cut into several parts. The content of polyvinyl acetate in the individual portions of the film differed by up to 20%, the largest differences being between the zones at the periphery of the circular film, on the one hand, and the zones in the middle, on the other hand.

Hence, no conclusions as to the composition of the whole film should generally be drawn from the analysis of separate portions of an inhomogeneous film. If inhomogeneity only existed in the microphases (externally

recognizable by a fine uniform turbidity of the film), the error would be relatively small. Things are different, however, when the film contains, in addition to microphases, different macrophases, which can be recognized by a spotted and streaky appearance of the film. It is therefore necessary in the latter case to homogenize the film prior to analysis, e.g., by mechanical crushing at low temperatures below the second-order transition temperature or by preparing a homogeneous solution of the film and atomizing the latter. The measure which is the most suitable must be determined in each case according to circumstances.

3. SEPARATION PROCESSES WITH MORE THAN TWO POLYMERS IN A SOLUTION

3.1. Aim of Tests

It was to be expected that, in the separation processes in the presence of more than two different polymers in the solution, phenomena appear which are, in principle, similar to those described in Section 1 for two polymers. Conditions are here more complicated, however, in that more than two phases may be formed among which the polymers are distributed according to nature, amount, and molecular weight. The study of these complicated separation processes is certainly fascinating for scientific reasons. Such separating tests are, moreover, also of immediate technical importance.

To solve these and similar problems we have therefore set ourselves the task of discovering the laws that regulate the distribution of the individual polymers among the layers formed in the separation into phases in triple polymer blends. The tests were also expanded to a system of four different polymers dissolved in a common solvent.

3.2 Starting Polymers, Systems Tested, Method of Separation

For the following separation tests, the polymers indicated in Table 1 were used. The polymer mixtures tested are listed in Table 2. The solutions were prepared in graduated cylindrical glass vessels with a base outlet. The same vessels were used as separation vessels so that losses due to transfer of the solution could be avoided. As the separating effects depend largely on the temperature, the vessels were kept in a room maintained at $22 \pm 2^\circ\text{C}$ until clear layers had been formed. This took 3 days in some cases. After separation into phases, the volumes of the individual layers

Table 1. Polymers Tested for the Separation into Phases

Polymer	η_{sp}/c
Polystyrene	1.57 in benzene ($c = 1\text{g}/100\text{ ml}$, 25°C)
Polyvinyl acetate	0.86 in benzene (c as above)
Polyvinyl chloride	1.93 in tetrahydrofuran (c as above)
Atactic polypropylene	0.48 in decahydronaphthalene ($c = 0.1\text{ g}/100\text{ ml}$, 135°C)

were read. The layers were then drawn off separately at the bottom and dried. The dry residues were weighed and chemically analyzed. In view of the inhomogeneity of the resulting films mentioned above in Section 2, the films were cut into small pieces for analysis, about 5 small pieces being used for each analysis.

3.3 Sources of Error

The tests suffer from several errors inherent in the method, which render it difficult to obtain exact analytical values. It is necessary to know the kind and extent of these errors in detail in order to know the degree to which conclusions can be drawn from the results. The main sources of error are the following:

- a) Nonsharp separation of the individual layers because a part of the layer always adheres to the glass wall and the outlet.
- b) In the evaporation of polymer solutions, inclusion of solvent residues must always be taken into account. As control tests with weight-in amounts of polymer have shown, this error can be substantially avoided by drying at a temperature about 20°C above the highest second-order transition temperature of the polymers present in the mixture.
- c) The greatest error is due to inhomogeneity of the film. This error was kept as small as possible by the measures described in Section 3.2.

These three errors are contained in the data given in the following tables. A comparison of the analytical values as well as of the results obtained by retests and a comparison between the weight-in quantity and the amount of polymer after dissolution and evaporation of the solvent show that the values indicated for the content of the individual polymers in the individual layers may have been falsified by $\pm 0.05\text{ g}$.

Table 2. Polymer Mixtures Tested^a

Test No.	Polymer (type and amount in grams)				Solvent		Number of layers formed
	PSt	PVAc	PVC	POP	Type	Amount (ml)	
1	1.5	1.5	3.0	—	THF	54	3
2	2.0	2.0	2.0	—	THF	54	3
3	2.3	2.3	1.4	—	THF	54	3
4	2.7	2.7	0.6	—	THF	54	3
5	2.8	2.8	0.4	—	THF	54	2
6	2.5	1.0	2.5	—	THF	54	3
7	1.0	2.5	2.5	—	THF	54	3
8	1.5	1.5	—	3.0	Benzene	54	3
9	2.0	2.0	—	2.0	Benzene	54	3
10	2.5	2.5	—	1.0	Benzene	54	3
11	2.7	2.7	—	0.6	Benzene	54	3
12	2.9	2.9	—	0.2	Benzene	54	2
13	1.0	2.5	—	2.5	Benzene	54	3
14	2.5	1.0	—	2.5	Benzene	54	3
15	2.5	2.5	2.5	2.5	THF	90	4

^aPSt = polystyrene, PVAc = polyvinyl acetate, PVC = polyvinyl chloride, POP = atactic polypropylene, and THF = tetrahydrofuran.

3.4. Results Obtained with Three Polymers

The test results are indicated in Tables 3 and 4. The figures in Column 2 of Tables 3 and 4 indicate the volume of the layers in milliliters and those in Column 3 indicate the amounts by weight of the polymers dissolved therein. From these values the concentration of the layers is calculated (Column 5). Columns 6, 7, and 8 contain the analytical results as the calculated weights of the three polymers in the individual layers. From the data of these tables the concentrations of the individual polymers in each layer and the percentage distribution of each polymer among the three layers has been calculated (Tables 5 and 6).

Table 3. Separation into Phases of the System PSt + PVAc + PVC in THF^a

Test No.	ml	g	g/ml	Amount of polymer (g)		
				PSt	PVAc	PVC
Lower layer						
1	35	3.2	0.09	0.2	0.4	2.65
2	25	2.4	0.095	0.15	0.5	1.8
3	14	1.15	0.08	0.05	0.15	1.0
4	3	0.25	0.085	<0.05	<0.05	0.2
5	0	0	—	Not measured		
6	30	2.6	0.085	0.2	0.25	2.15
7	30	2.6	0.085	0.15	0.4	2.05
Middle layer						
1	13	1.4	0.11	0.15	1.0	0.2
2	16.5	1.6	0.095	0.15	1.35	0.1
3	23	2.35	0.1	0.2	1.9	0.25
4	30	3.05	0.1	0.3	2.5	0.3
5	32	3.3	0.105	Not measured		
6	8	0.9	0.11	0.1	0.6	0.15
7	22	2.45	0.11	0.15	2.0	0.3
Upper layer						
1	12	1.4	0.115	1.15	0.1	0.15
2	18.5	2.0	0.11	1.7	0.15	0.1
3	23	2.5	0.11	2.05	0.25	0.15
4	27	2.7	0.10	2.4	0.2	0.1
5	28	2.7	0.095	Not measured		
6	22	2.5	0.115	2.2	0.15	0.2
7	8	0.95	0.12	0.7	0.1	0.15

^aSee Table 2 for meaning of abbreviations.

Table 4. Separation into Phases of the System PSt + PVAc + POP in Benzene^a

Test No.	ml	g	g/ml	Amount of polymer (g)		
				PSt	PVAc	POP
Lower layer						
8	15	1.5	0.1	0.1	1.25	0.1
9	20	2.0	0.1	0.15	1.8	0.1
10	24	2.5	0.105	0.2	2.2	0.1
11	27	2.8	0.105	0.2	2.6	0
12	30	3.1	0.105	Not measured		
13	32	3.3	0.105	0.55	2.4	0.4
14	14	1.3	0.095	0.3	0.75	0.25
Middle layer						
				Not measured		
8	20	2.05	0.1	1.35	0.15	0.5
9	26	2.5	0.095	1.8	0.2	0.6
10	30	2.95	0.1	2.3	0.25	0.4
11	29	2.75	0.095	2.5	0.1	0.2
12	30	2.9	0.095	Not measured		
13	10	1.0	0.1	0.45	0.1	0.45
14	26	2.8	0.11	2.15	0.15	0.5
Upper layer						
8	25	2.45	0.1	0.05	0.1	2.35
9	14	1.5	0.105	0.05	0.05	1.4
10	6	0.55	0.090	0	0.05	0.5
11	4	0.45	0.11	<0.05	0	0.4
12	0	0	—	Not measured		
13	18	1.7	0.095	0	0.05	1.65
14	20	1.9	0.095	0.05	0.1	1.75

^aSee Table 2 for meaning of abbreviations.

Table 5. Assessment of Data of Table 3, Distribution of the Polymers between the 3 Phases^a

Test No.	Concentration in layer (g/100 ml)			% of used polymer in layer		
	PSt	PVAc	PVC	PSt	PVAc	PVC
Lower layer						
1	0.55	1.15	7.55	13.5	26.5	88.5
2	0.60	2.0	7.2	7.5	25.0	90.0
3	0.35	1.05	7.15	2.0	6.5	71.5
4	~1	~1	6.75	<2	<2	33.5
5	Not measured			Not measured		
6	0.65	0.85	7.2	8.0	25.0	86.0
7	0.5	1.35	6.8	15.0	16.0	82.0
Middle layer						
1	1.15	7.7	1.55	10.0	66.5	6.5
2	0.9	8.2	0.6	7.5	67.5	5.0
3	0.85	8.3	1.1	9.0	82.5	18.0
4	1.0	8.3	1.0	11.0	92.5	50.0
5	Not measured			Not measured		
6	1.25	7.5	1.9	4.0	60.0	6.0
7	0.7	9.1	1.35	15.0	80.0	12.0
Upper layer						
1	9.6	0.85	1.25	76.5	7.0	5.0
2	9.2	0.8	0.55	85.0	7.5	5.0
3	8.9	1.1	0.65	89	11.0	10.5
4	8.9	0.75	0.35	89	7.5	16.5
5	Not measured			Not measured		
6	10.0	0.7	0.9	88.0	15.0	8.0
7	8.8	1.25	1.85	70.0	4.0	6.0

^aSee Table 2 for meaning of abbreviations.

Table 6. Assessment of Data of Table 4, Distribution of the Polymers between the 3 Phases^a

Test No.	Concentration in layer (g/100 ml)			% of used polymer in layer		
	PSt	PVAc	POP	PSt	PVAc	POP
Lower layer						
8	0.65	8.35	0.65	6.5	83.5	3.5
9	0.75	9.0	0.5	7.5	90.0	5.0
10	0.85	9.2	0.4	8.0	88.0	10.0
11	0.75	9.6	0	7.5	96.5	0
12	Not measured			Not measured		
13	1.7	7.5	1.25	55	96.0	16.0
14	2.15	5.35	1.8	12.0	75.0	10.0
Middle layer						
8	6.75	0.75	2.75	90.0	10.0	18.5
9	6.9	0.75	2.3	90.0	10.0	25.0
10	7.65	0.85	1.35	92.0	10.0	40.0
11	8.6	0.35	0.7	92.5	3.5	33.5
12	Not measured			Not measured		
13	4.5	1.0	4.5	45	4.0	18.0
14	8.25	0.6	1.9	86.0	15.0	20.0
Upper layer						
8	0.2	0.4	9.4	3.5	6.5	78.0
9	0.35	~0.2	10.0	2.5	<2	70.0
10	0	0.85	8.35	0	2.0	50.0
11	~ 0.1	0	10.0	0	0	66.5
12	Not measured			Not measured		
13	0	~0.2	9.2	0	<1	66.0
14	0.25	0.5	8.75	2.0	10.0	70.0

^aSee Table 2 for meaning of abbreviations.

3.4.1. Solutions of Polystyrene + Polyvinyl Acetate + Polyvinyl Chloride in Tetrahydrofuran. The following correlations can be seen from Tables 3 and 5:

a) According to the data of Table 3, the total concentrations of the three polymers in each layer are about equal to the polymer concentration of the total system and are about 0.1 g in 1 ml, almost independent of the mixing ratio of the polymers.

b) In almost all cases each layer contains a partial amount of each polymer.

c) Each of the three layers formed is distinguished from the others by the fact that a specific polymer has been accumulated therein in preference to the other polymers. This applies even to cases in which one of the polymers constitutes only one-sixth or even less of the total amount of polymers used (cf. Tests 4, 6, and 7).

d) The order of the layers depends on the density of the layers.

e) The layer rich in polyvinyl chloride always contains more polyvinyl acetate than polystyrene (cf. Table 5).

f) The layer rich in polyvinyl acetate contains more polyvinyl chloride than polystyrene (cf. Table 5) in almost all cases.

g) Of the concentrations of the three polymers in the individual layers, that of the polymer having the highest concentration in the layer varies least with the mixing ratio (cf. Columns 2, 3, and 4 of Table 5).

h) The quantitative distribution of one polymer among the three layers depends largely on the initial mixing ratio (cf. Columns 5, 6, and 7 of Table 5). This dependence is less pronounced for the polymer accumulated in the highest concentration in a layer.

i) If the total mixture contains less than about 7% polyvinyl chloride (Test 5), only two layers are formed because the small amount of polyvinyl chloride is compatible with the other polymers and is distributed between the two layers.

3.4.2. Solutions of Polystyrene + Polyvinyl Acetate + Atactic Polypropylene in Benzene. The following correlations can be gathered from Tables 4 and 6:

a) Like 3.4.1.a.

b) Like 3.4.1.b.

c) Like 3.4.1.c; the remarks on the distribution of the polymers apply also to the case in which one of the polymers constitutes only one-sixth or less of the total amount of polymers (cf. Tests 10, 11, 13, and 14).

- d) Like 3.4.1.d.
- e) The layer rich in polyvinyl acetate contains more polystyrene than polypropylene (cf. Table 6) in almost all cases.
- f) The layer rich in polystyrene always contains more polypropylene than polyvinyl acetate (cf. Table 6).
- g) The layer rich in polypropylene contains particularly small amounts of polystyrene and polyvinyl acetate (cf. Table 6).
- h) Of the concentrations of the three polymers in the individual layers, that of the polymer present in the highest concentration in the layer varies least with the mixing ratio (cf. Columns 2, 3, and 4 of Table 6).
- i) Like 3.4.1.h (cf. Columns 5, 6, and 7 of Table 6).
- j) If the total mixture contains less than about 3.5% polypropylene (Test 12), only two layers are formed because the small amount of polypropylene is compatible with the other polymers and is distributed between the two layers.

3.4.3. Molecular-Physical Explanation of Some Results. The distribution of the three polymers among the three layers is above all regulated by the forces acting between the solvated macromolecules of like or different nature. In any discussion the following factors as deduced from the known conceptions of the reciprocal action between molecules must be considered:

- a) Only nonpolar dispersion forces, the strength of which depends on the polarizability, act between the polypropylene molecules.
- b) Only nonpolar dispersion forces, which are somewhat stronger than in the case of polypropylene, act between the polystyrene molecules because of the higher polarizability of the benzene rings and their partial reciprocal orientation.
- c) In addition to dispersion forces, dipole forces, the strength of which depends on the magnitude of the dipole moment and the degree of accessibility of the dipoles, also act between the polyvinyl acetate molecules. The reciprocal action is therefore on the whole stronger than with polypropylene or polystyrene.
- d) In addition to dispersion forces, dipole forces, which are somewhat stronger than in the case of polyvinyl acetate because of the dipoles being more easily accessible, also act between the polyvinyl chloride molecules.
- e) The dispersion forces between polypropylene and polystyrene are smaller than those between macromolecules of the same kind because of the different structure of the partners.
- f) Dispersion forces as well as inductive forces act between polypropylene and polyvinyl acetate. The sum of the two forces is relatively small.

g) The forces between polypropylene and polyvinyl chloride are the same as those set forth in Section 3.4.3.f. These forces are, however, weaker than those between polypropylene and polyvinyl acetate for the reasons set forth in Section 3.4.3.d.

h) The forces between polystyrene and polyvinyl acetate are stronger than those between polypropylene and polyvinyl acetate, as the inductive forces between the C=O dipole of polyvinyl acetate and the polystyrene are more pronounced because of the higher polarizability of the benzene rings.

i) The forces between polystyrene and polyvinyl chloride are stronger than those between polypropylene and polyvinyl chloride mentioned in Section 3.4.3.g because of the inductive forces described in Section 3.4.3.h, but are smaller than those between polystyrene and polyvinyl acetate for the reasons mentioned in Section 3.4.3.d (particularly strong reciprocal action between the dipoles of the polyvinyl chloride molecules).

j) The forces between polyvinyl acetate and polyvinyl chloride are stronger than those mentioned in Sections 3.4.3f, 3.4.3.g, 3.4.3.h, and 3.4.3.i. They are, however, smaller than the forces between the polyvinyl acetate as well as between the polyvinyl chloride molecules themselves.

These qualitative details may be used for explaining some of the experimental results mentioned in Sections 3.4.1 and 3.4.2.

It is evident from what has been set forth above that each polymer must be contained in each layer because of the reciprocal forces acting between all kinds of polymers, regardless of whether the latter are of the same or of different nature (see Sections 3.4.1.b and 3.4.2.b).

The accumulation of a specific polymer type in preference to another in a specific layer (see Sections 3.4.1.c and 3.4.2.c) is above all due to the fact that the intermolecular forces between the macromolecules of the same kind are stronger than those between the different macromolecules. As the forces between polyvinyl acetate and polyvinyl chloride are stronger than those between polyvinyl acetate and polystyrene (see Sections 3.4.3.h and 3.4.3.j) and the latter are in turn stronger than those between polystyrene and polyvinyl chloride (see Section 3.4.3.i), the relative distribution of polystyrene, polyvinyl acetate, and polyvinyl chloride among the three layers as indicated above (Sections 3.4.1.e and 3.4.1.f) takes place. In analogous manner, the forces between polystyrene and polypropylene are stronger than those between polystyrene and polyvinyl acetate (see Sections 3.4.3e and 3.4.3.f), and the latter are stronger than those between polyvinyl acetate and polypropylene (see Section 3.4.3.f). This results in

the relative distribution of polystyrene, polyvinyl acetate, and polypropylene among the three layers as indicated in Sections 3.4.2.e and 3.4.2.f. The relatively small reciprocal action between polypropylene and polystyrene and between polypropylene and polyvinyl acetate, respectively, (see Sections 3.4.3.e and 3.4.3.f) accounts for the phenomenon mentioned in Section 3.4.2.g.

3.5. Results Obtained with Four Polymers

The mixture of polystyrene + polyvinyl acetate + polyvinyl chloride + atactic polypropylene in tetrahydrofuran (cf. Test 15, Table 2) was subjected to only one separation test. The results obtained are indicated in Tables 7 and 8. From the data given in these tables, the following can be gathered:

- a) As has been expected, each layer contains all polymers.
- b) The total concentration of the four polymers in each layer is about 0.1 g/1 ml solution in each layer.
- c) In each layer a specific polymer is contained in a higher concentration than the other polymers.
- d) The layer rich in polyvinyl chloride contains more polyvinyl acetate than polystyrene or polypropylene.
- e) The layer rich in polyvinyl acetate contains more polystyrene than polypropylene.
- f) The layer rich in polystyrene contains more polypropylene than polyvinyl acetate or polyvinyl chloride and more polyvinyl acetate than polyvinyl chloride.

These results correspond completely to those given in Section 3.4. for the triple polymer blends. They can be explained as described in Section 3.4.3.

4. SEPARATION PROCESSES IN A SYSTEM COMPRISING TWO POLYMERS, A COMMON SOLVENT, AND A NONSOLVENT FOR ONE OF THE POLYMERS

As we have shown in an earlier article [2], the limit concentration c_{gr} mentioned in Section 2, above which two different polymers become partially incompatible in solution, depends largely on the nature of the solvent. The better the macromolecules are solvated by the solvent molecules,

Table 7. Separation into Phases of the System PSt + PVAc + PVC + POP in THF^a

Layers	ml	g	g/100 ml	Amount of polymers (g)			
				PSt	PVAc	PVC	POP
1st layer (bottom layer)	23	2.2	0.095	0.35	1.5	0.2	0.2
2nd layer	35	3.4	0.095	0.4	0.55	2.0	0.4
3rd layer	26	2.8	0.11	1.7	0.4	0.25	0.5
4th layer (top layer)	15	1.55	0.105	0.05	0.05	0.05	1.4

^aSee Table 2 for meaning of abbreviations.

Table 8. Assessment of Data of Table 7, Distribution of the Polymers between the 4 Phases^a

Layers	Concentration in layer (g/100 ml)				% of used polymer in layer			
	PSt	PVAc	PVC	POP	PSt	PVAc	PVC	POP
1st layer (bottom layer)	1.5	6.55	0.85	0.85	14.0	60.0	8.0	8.0
2nd layer	1.15	1.55	5.7	1.15	16.0	22.0	80.0	16.0
3rd layer	6.55	1.55	0.95	1.9	68.0	16.0	10.0	20.0
4th layer (top layer)	3.5	3.5	3.5	9.3	2.0	2.0	2.0	56.0

^a See Table 2 for meaning of abbreviations.

the better is their compatibility with macromolecules of different structure and the higher is c_{gr} . However, the quality of a solvent may be deteriorated by the addition of a nonsolvent for one of the polymers. If the starting solution of the polymer mixture is slightly turbid, i.e., if the process is carried out with concentration c_{gr} at the very limit of compatibility, the following three possibilities exist for the action of a nonsolvent on the total mixture:

a) By the dilution the total concentration of the polymers is reduced, compatibility is consequently improved, and the solution becomes completely clear.

b) The nonsolvent produces a partial desolvation whereby c_{gr} is reduced and the solution becomes very turbid because of the now increased incompatibility. When the mixture is allowed to stand, two clear layers are formed.

c) Desolvation is so pronounced that one of the polymers is precipitated, i.e., turbidity occurs upon the addition of the nonsolvent, but when the solution is allowed to stand the precipitated polymer separates from the turbid solution in a strongly swollen form.

All three cases are possible. Polystyrene and polyvinyl acetate dissolved in tetrahydrofuran as the common solvent, were used as polymers. By using 0.7 g of each polymer and 22.3 ml tetrahydrofuran, a solution was obtained which was almost clear at room temperature; c_{gr} was therefore 5.95 g/100 ml solution. On the addition of 7.2 ml cyclohexane, in which polyvinyl acetate is completely insoluble, the solution became strongly turbid. From this it follows that turbidity was caused by the reduction of c_{gr} on the addition of the cyclohexane, i.e., by a deterioration of the compatibility of the two types of polymer, the reduction of c_{gr} being chiefly the result of the partial desolvation of the polyvinyl acetate molecules. Hence, the result was case b) mentioned above. When a further 7.9 ml cyclohexane were added, the turbid solution became clear again since the total concentration of the polymers in the solution had been reduced by the dilution to 3.6 g/100 ml solution and this concentration was smaller than the c_{gr} value of the mixture which was 3.8 g/100 ml solution as determined by control tests. Thus complete compatibility prevailed again in the total mixture (case a)). When the mixture was finally diluted with a further 15 ml cyclohexane, turbidity appeared (case c)) with precipitation of polyvinyl acetate which was pure as determined by IR spectroscopy (polystyrene did not precipitate under these conditions).

The above example has been presented as a warning. When at least two different polymers which are dissolved in a common solvent are used, unexpected phenomena may appear when a nonsolvent for one of the polymers is added, in order, e.g., to separate one type of polymer. These phenomena may lead to false reasoning if they are not taken into consideration. They are due to the production of several effects that may have opposite actions.

REFERENCES

- [1] O. Fuchs, *Angew. Makromol. Chem.*, **1**, 29 (1967).
- [2] O. Fuchs, *Makromol. Chem.*, **90**, 293 (1966).

O. Fuchs

*Farbwerke Hoechst A.G.,
Vormals Meister Lucius & Brüning
Frankfurt am Main, West Germany*

*Accepted by editor August 12, 1970
Received for publication August 14, 1970*