Continuous Fractionation and Solution Properties of PIB.* II. CPF Optimization

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Synopsis

The quality of polymer fractionation depends on the choice of the mixed solvent as well as on the particular conditions of operating the continuous countercurrent extraction. With a polyisobutylene (PIB) sample of medium molecular weight (M_w = 98,400 g/mol and $U = (M_w/M_n) - 1$ = 1.4) plus the mixed solvents toluene/2-butanone (TOL/MEK) and n-heptane/2-butanone (HEP/MEK) (both giving comparably good fractionation in equilibrium experiments), possible ways to optimize the CPF were tested. The mixed solvent HEP/MEK turns out to be superior to TOL/MEK for kinetic reasons. Due to the larger gap between its density and that of the pure polymer, the coexisting phases can still move through the column, even if the working point of the CPF is chosen close to the consolute point of the ternary system. Under these conditions the mass transfer becomes more rapid, and up to 80% of the (mixed) solvent can be economized as compared with TOL/MEK. Four CPF runs with TOL/MEK (each dividing the polymer material into portions approximately equal in weight, and rejecting the first low molecular fraction) yielded four 200 g samples of M_w ranging from 80,600 to 257,000 with U values of ca. 0.3.

INTRODUCTION

In case a polymer cannot be synthesized with narrow molecular weight distribution, fractionation is the only way to achieve such a material. There exist numerous methods to fractionate polymers in a gram scale,[2,3] but not in a kilogram scale. For this, practically, only a continuous countercurrent extraction comes into question. But, according to examinations of Dobry,[4] the partition of the polymer molecules according to their chain lengths between two immissible low molecular liquids turned out to be impracticable. For this reason the CPF[5,6] makes use of the miscibility gap between the polymer and a suitable mixed or single (theta) solvent.

In Part I[1] of this series we have described experiments and criteria to detect the most apt mixed solvent for the application of the CPF and reported on first results with this method using a PIB sample with M_w = 420,000.

In order to find out the operating conditions under which full use of the separating power of the CPF can be made, systematic runs were made with comparatively low molecular weight PIB and the thermodynamically best suited solvent/nonsolvent mixture, toluene/methyl ethyl ketone (cf. Part I[1]). Furthermore, experiments were carried out with a second mixed solvent (of thermodynamically comparable fractionation aptitude) but sufficiently great

*Part I: cf. Ref. 1.

difference in its density to the pure polymer so that experiments can be performed closer to the consolute point of the ternary system.

Principle of the CPF[5,6]

In the following, the principle of the CPF will be explained for the normally used mixed solvent.

The polymer (index 3) is dissolved in a solvent (index 1)/nonsolvent (index 2) mixture and this solution (feed = FD) is extracted by a second liquid (extracting agent = EA) which contains the same mixed solvent as the feed.

The solvent components and the composition of FD and EA are chosen such that

  (i)   the low molecular weight liquids are miscible over the whole concentration range,
 (ii)   the entire system formed by the starting polymer and the mixed solvent exhibits a miscibility gap at the temperature of operation,
(iii)   the composition of the FD corresponds to a point outside of this miscibility gap in the Gibb's phase triangle, and
 (iv)   that the straight line drawn between FD and EA (working line) intersects the miscibility gap.

The CPF is then performed such that the working point (composition of the entire content in the column) is situated within the two-phase region. The situation is shown in Figure 1.

If these requirements are fulfilled and the corresponding flows $\dot{V}$ of FD and EA are selected properly, the FD (depleted of the short polymer chains) leaves the countercurrent column as the polymer-rich phase (gel = GL) and the EA (now containing the short polymer chains) as the polymer-poor phase (sol = SL). This means that the fractionation is achieved by the fact that the
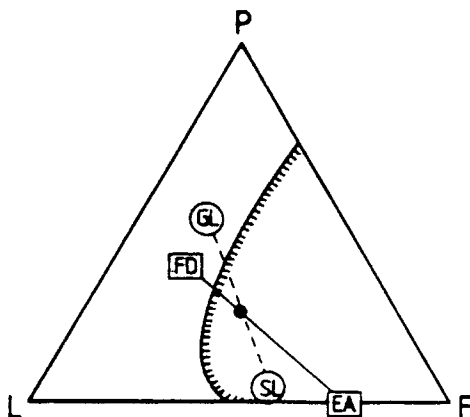

Fig. 1. Schematic representation of the continuous polymer fractionation (CPF) in a Gibbs phase triangle (P = polymer, F = precipitant, L = solvent) showing the typical composition of the phases entering (FD = feed, EA = extracting agent) and leaving (GL = gel, SL = sol) the countercurrent column: (●) composition of the entire content in the column (working point).

polymer molecules distributed themselves on the countercurrent phases according to their chain length.

The subdivision of the original polymer on the coexisting phases, expressed by $\dot{G} = \dot{m}_3^{SL}/\dot{m}_3^{GL}$, can be regulated by the nonsolvent/solvent ratio in the extracting agent (w_2^{EA}, w = weight fraction) and by the ratio of the flows entering the column, $\dot{q} = \dot{V}^{EA}/\dot{V}^{FD}$

In the case of stationary states the following balance equations must be valid:

$$\dot{X}^{FD} + \dot{X}^{EA} = \dot{X}^{GL} + \dot{X}^{SL} \tag{1}$$

$$M_w^{FD} \cdot \dot{m}_3^{FD} = M_w^{SL} \cdot \dot{m}_3^{SL} + M_w^{GL} \cdot \dot{m}_3^{GL} \tag{2}$$

where $\dot{X}$ stand for $\dot{V}$, $\dot{V}_i$ (flux of volume), or $\dot{m}_i$ (flux of mass), i indicates the components of the ternary system, and M_w is the weight average molecular weight. Using $\dot{G}$ instead of $\dot{m}_3$, eq. (2) can also be written in the following manner:

$$M_w^{FD}(\dot{G} + 1) = M_w^{GL} + M_w^{SL} \cdot \dot{G} \tag{3}$$

The difference between the classical extraction and the CPF (intrinsic extraction) is most clearly demonstrated by the fact that the CPF can be carried out even in a single (theta) solvent. In this case the miscibility gap in the Gibb's phase triangle is replaced by the cloud-point curve (T_{cp} vs. wt % polymer). The working line is then fixed by the working temperature T_0 and the respective working point by the flow ratio $\dot{q} = \dot{V}^{EA}/\dot{V}^{FD}$ just as with the CPF in a ternary system (cf. Fig. 2).

EXPERIMENTAL

Materials

Starting material for the CPF was Oppanol B 15 (BASF, Ludwigshafen, West Germany), abbreviated PIB II (cf. Part I[1]), with the following character-
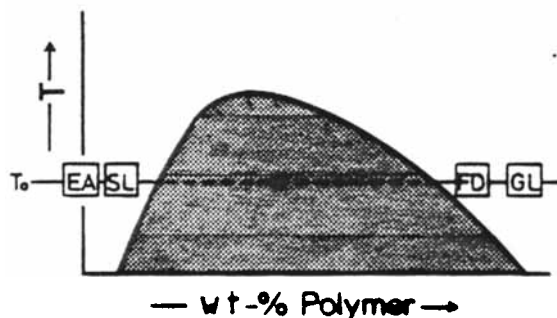

Fig. 2. Scheme of the continuous polymer fractionation in the special case of a binary system showing the typical composition of the phases entering and leaving the countercurrent column. The two-phase region is indicated by the shaded area: (●) working point; T = cloud-point temperature; T_0 = working temperature.

istic data: $M_{GPC}^{max} = 73{,}200$, $M_w = 98{,}400$, and nonuniformity $U = (M_w/M_n) -$
$1 = 1.4$. As solvent components toluene (TOL) and n-heptane (HEP) and as
nonsolvent 2-butanone (MEK) were used. For further information see Table I
of Part I.[1]

Procedure

CPF. For fractionation a fully thermostatted sieve-bottom column with
pulsator (Fa. Quickfit, Wiesbaden, West Germany) was used. The separating
column with a length of 100 cm, an inside diameter of 2.5 cm, and a volume of
500 cm^3 (total volume of the apparatus: 2500 cm^3) contains an insertion of
super-refined steel with 19 sieve bottoms (each with 7% of the surface area
occupied by pores). A pump permits a pulsation from 0 to 60 cm^3 (linearly
scaled from 1 to 20) with a frequency from 0 to 2.5 s^{-1} (linearly scaled from 1
to 10). For the transportation of FD and EA, valveless FMI wobble plunger
pumps were used. The flux of volumes of FD and EA were read off from a
calibration on the corresponding reservoirs which are also thermostatted. The
flux of SL was determined by collecting it into a graduated cylinder, the flux
of GL from its mass and density and the flux of masses ($\dot{m}_3$) by drying small
samples of both phases with a vacuum pump at ca. 60°C. The complete CPF
apparatus is shown in Figure 3.

Sample Preparation

For drying the CPF samples, the solvent components were removed by
using a rotating evaporator and a water jet vacuum pump. After that, the
samples were dissolved in cyclohexane, dried once more by the same proce-
dure, and then dissolved in cyclohexane again. The concentrated solution was
frozen using liquid nitrogen and dried in an evacuated drying oven at room
temperature for a week. By this procedure, the material "exploded," giving a
relatively porous structure, which, however, gradually disappears within a few
days by creeping, in contrast to the higher molecular weight material of Part
I,[1] where this process takes up to several weeks.

Cloud-Point Titration, GPC, Light Scattering

For experimental detail concerning these techniques, see the Experimental
section of Part I.[1]

RESULTS AND DISCUSSION

As previously mentioned in the Introduction, a polymer with a molecular
weight on the order of 100,000 is much better suited for systematic experi-
ments with regard to optimization of the working parameters than the high
molecular weight polymer used in Part I.[1] The reason for this is that one can
attain a larger range of $\dot{G}$ values (especially $\dot{G} < 1$) with a lower molecular
weight sample.

Because of the fact that the CPF of PIB I ($M_w = 420{,}000$; cf. Part I[1]) leads
to an unusual consistency of the gel phase (curdlike suspensions instead of
droplets), first experiments with PIB II were carried out with the mixed
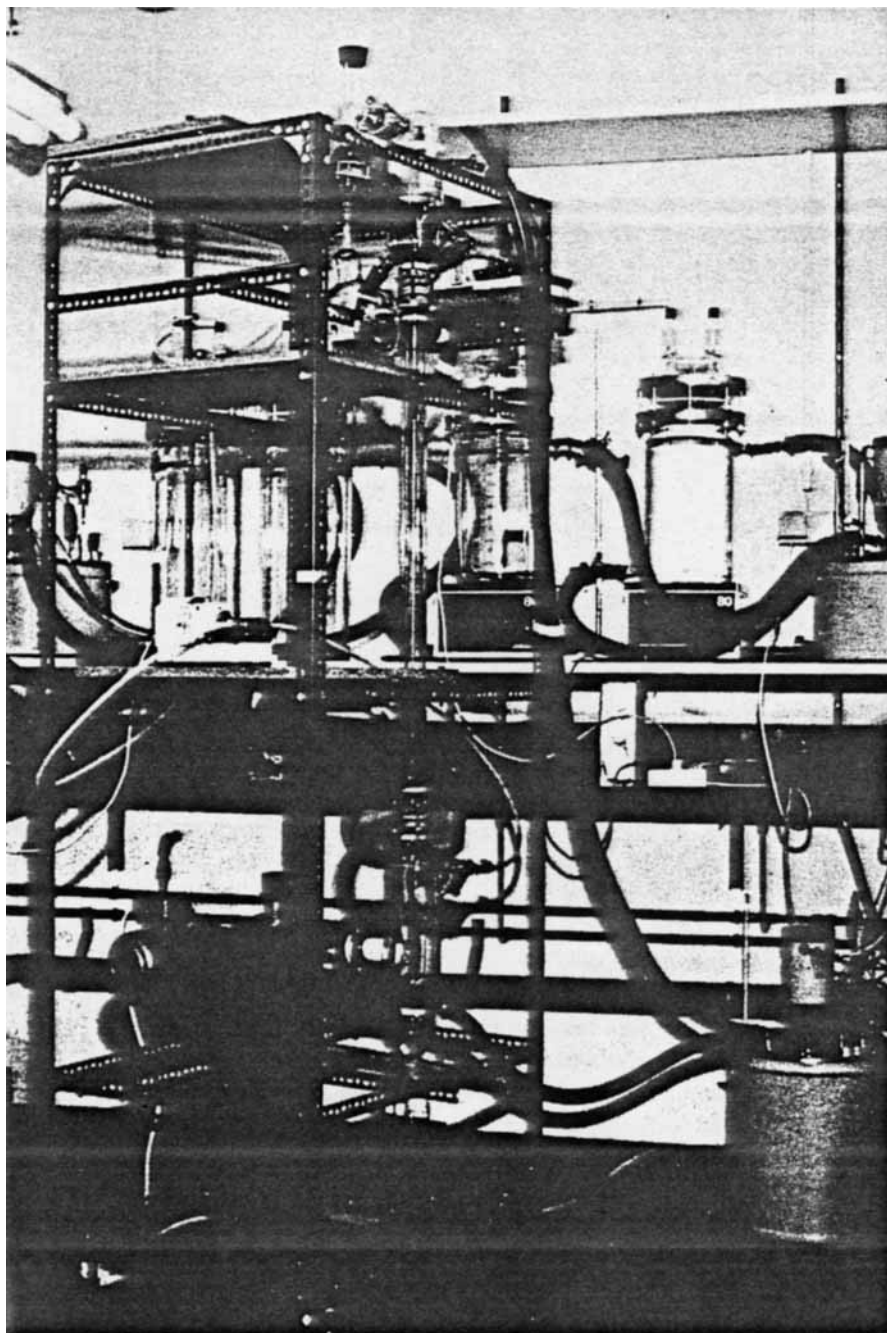solvent TOL/MEK.

Fig. 3. Photograph of the CPF apparatus. The stand contains the countercurrent sieve bottom column with pulsator and separating vessels on either end. The pump for the transport of extracting agent is located on the middle shelf. The shelf behind the apparatus contains the thermostatted reservoirs for feed (on magnetic stirrers) and for extracting agent.
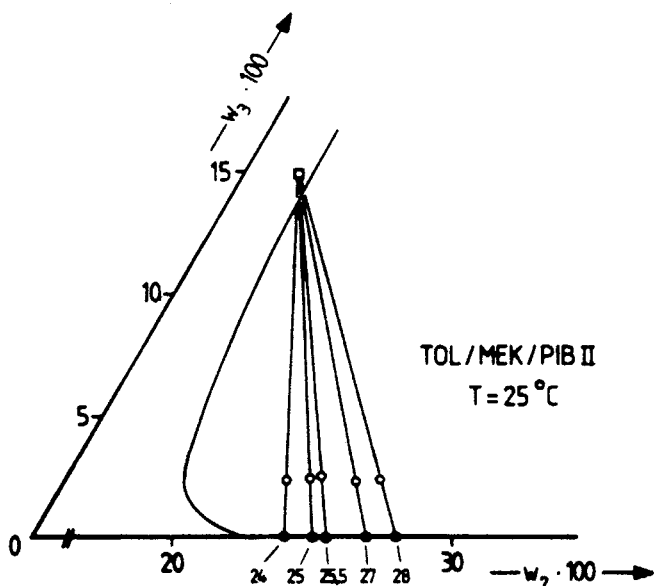
Fig. 4. Phase diagram of the system toluene/methyl ethyl ketone/PIB II at 25°C and working lines of the experiments collected in Table I: w_i = weight fraction of component i; (□) feed; (●) extracting agent; (○) working point.

CPF in the mixed solvent TOL / MEK

In addition to the consistency of the gel phase, the most important question in this section is: what nonuniformity U of the fractions can be realized in three preparative CPF runs, each with $\dot{G} \approx 1$, starting with a material of $U = 1.4$?

Variation of w_2^{EA}. Starting from the phase diagram shown in Figure 4, the influence of the composition of extracting agent was determined at a flow ratio $\dot{q} \approx 5$ using a feed with 15 wt % polymer and $\dot{m}_3^{FD}$ of ca. 0.65 g/min. Experimental parameters and results are listed in Table I.

With increasing concentration of the nonsolvent in the EA (w_2^{EA} = 0.24–0.28) the weight ratio $\dot{G}$ of the polymers leaving the column in the sol and in the gel phase decreases from 1.84 to 0.33 (cf. Fig. 5), that is, the further the working point lies inside the miscibility gap, the more PIB will leave the column in the gel phase.

The very good mass balances (cf. columns $\dot{m}_3^{FD}$ and $\dot{m}_3^{GL} + \dot{m}_3^{SL}$ of Table I) show that in all experiments a stationary state could be reached.

In contrast to the CPF of the higher molecular weight PIB I sample (cf. Part I[1]) the gel phase in the column consists of droplets of about 2 mm diameter on an average.

As shown in Figure 6 the molecular weights M_{GPC}[†] of the polymers contained in the coexisting phases increase with increasing $\dot{G}$ value. At the highest $\dot{G}$ value of 1.88 M_{GPC}^{GL} is about twice as large as M_{GPC}^{FD}.

[†] The calculation of M_w^{SL} from the GPC eluation curve turned out to be impossible, because of the fact that the peak resulting from the stabilizer (all Oppanols contain 1000 ppm 2,6-di-*tert*-butyl-4-methylphenole) overlaps the low molecular tailing of the polymer. For this reason only M_{GPC} values (maximum of the GPC curve) could be determined.

TABLE I
Fractionation of PIB II in the Mixed Solvent TOL/MEK—Variation of u_2^{EA}

(a) Working parameters: $T = 25°C$

No.	u_2^{FD}	u_3^{FD}	u_2^{EA}	$\dot{V}^{FD}$ (cm³/min)	$\dot{q}$	$\dot{m}_3^{FD}$ (g/min)	A	ν	M_w^{FD}	M_{GPC}^{FD}	$b_{1/2}^{FD*}$ (cm)	U^{FD}
1	0.168	0.150	0.240	4.75	5.5	0.614	7	3.0	98,400	73,200	3.5	1.4
2	0.168	0.150	0.250	5.0	5.3	0.647	5	3.5	98,400	73,200	3.5	1.4
3	0.168	0.150	0.255	5.2	5.0	0.672	5	3.5	98,400	73,200	3.5	1.4
4	0.168	0.150	0.270	5.0	5.5	0.647	5	3.5	98,400	73,200	3.5	1.4
5	0.168	0.150	0.280	5.0	5.3	0.647	5	3.5	98,400	73,200	3.5	1.4

(b) Experimental results

| No.	$\dot{V}^{GL}$ (cm³/min)	$\dot{V}^{SL}$ (cm³/min)	u_3^{GL}	u_3^{SL}	$\dot{m}_3^{GL}$ (g/min)	$\dot{m}_3^{SL}$ (g/min)	$\dot{m}_3^{GL}+\dot{m}_3^{SL}$ (g/min)	$\dot{G}$	M_{GPC}^{GL}	$b_{1/2}^{GL}$ (cm)	M_{GPC}^{SL}	$b_{1/2}^{SL}$ (cm)
1	1.22	29.8	0.206	0.0157	0.217	0.399	0.616	1.84	131,000	2.50	53,100	2.95
2	1.65	29.9	0.220	0.0131	0.312	0.332	0.644	1.05	118,000	2.59	46,400	2.80
3	1.86	29.5	0.239	0.0114	0.383	0.286	0.669	0.75	100,000	2.70	38,400	2.75
4	1.95	30.6	0.264	0.0075	0.444	0.195	0.639	0.43	91,000	2.83	33,400	2.67
5	2.09	29.4	0.270	0.0064	0.486	0.160	0.646	0.33	86,000	2.90	29,000	2.60

a Halfwidth of the GPC elution peak.
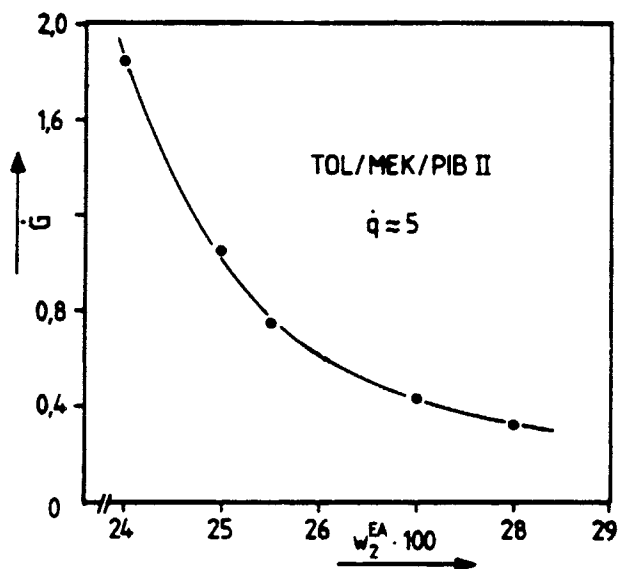
Fig. 5.   System TOL/MEK/PIB II: weight ratio $\dot{G}$ of the polymer leaving the column in the sol and in the gel, as a function of the weight fraction of nonsolvent in the extracting agent at the ratio of the flows entering the column of ca. $\dot{q} = 5$ and a polymer concentration in the feed of 15 wt %.

Preparative Fractionation in Three Steps. The working parameters of experiment no. 2 (cf. Table I) were chosen for the first step of the preparative CPF. During a fractionation time of 2 × 24 h, 2000 g PIB II were fractionated yielding SL I and GL I. The resulting $\dot{G}$ value of 1.05 was identical with that of experiment no. 2.

While the sol I was not fractionated further, the composition of GL I was modified slightly.

Before starting each next step, a small quantity of the polymer material to be refractionated was separated and dried and its phase diagram determined. This knowledge of the phase diagram as well as some fundamental results of earlier experiments (for example, decrease of w_2^{EA} with increasing molecular weight of the starting polymer) made it possible to find out suitable working parameters for the CPF within about 3 h.

The complete experimental parameters and results of all preparative runs are listed in Table II. The three fractionation steps performed four PIB samples (of ca. 200 g each) with M_w values between 80,000 and 260,000 and nonuniformities of about 0.25. For illustration, the course of the experiments is represented schematically in Figure 7 together with the normalized GPC curves for the original polymer PIB II and for the different fractions.

The comparison of the present separation effects with those observed with PVC[6] shows less favorable results for PIB in spite of the fact that all experiments proceeded without any technical problems. This result is surprising since the fractionation of PVC required a thermodynamically very different solvent–nonsolvent pair in order to hinder the formation of associates via intersegmental contacts.

The unsatisfactory separation of PIB II in the mixed solvent TOL/MEK seems to be the extraordinary stability of the gel droplets which hinders the
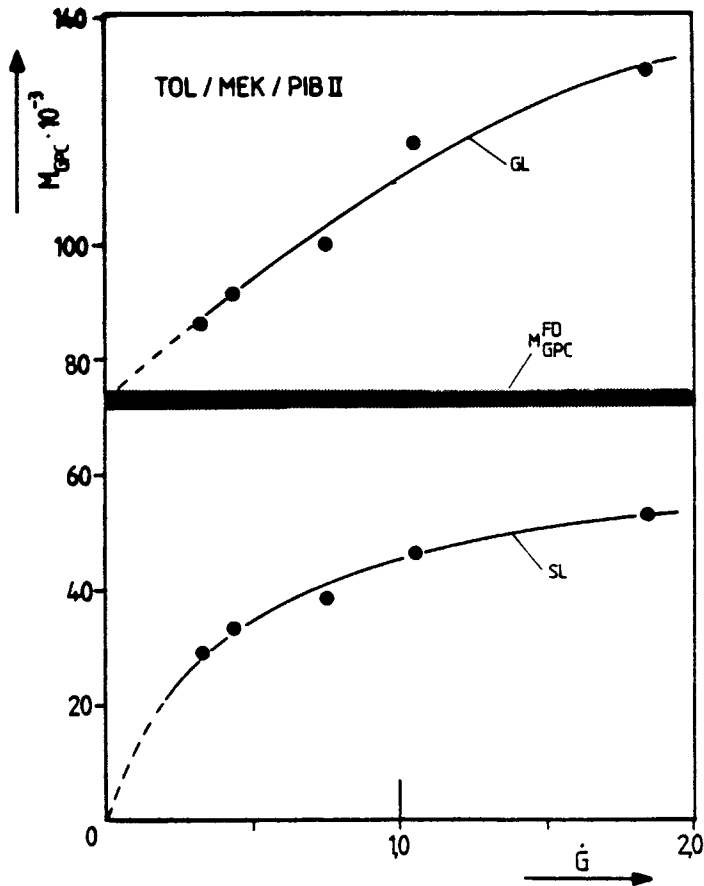
Fig. 6. System TOL/MEK/PIB II molecular weights M_{GPC} (maximum of the GPC eluation curve) of the polymers leaving the column in the sol and in the gel as a function of the weight ratio $\dot{G} = \dot{m}_3^{SL}/\dot{m}_3^{GL}$. For comparison, M_{GPC} of the starting material PIB II is indicated by the shaded band.

exchange of polymer molecules of different chain length between the counter-current phases. An improvement of the degree of dispersion can normally be reached by a higher frequency (ν) or amplitude (A) of pulsation.

However, in the present case the increase of A from 5 to 15 did not lead to a better dispersion, but to damming up in the separating column. A noticeable dispersion of droplets in the column could only be reached at the highest A value of 20 (cf. Experimental section), but at this amplitude practically the total feed flooded over the top of the column.

The high stability of the gel droplets can be interpreted as a consequence of the high interfacial tension between the coexisting phases; its reduction should, in principle, be possible by a proper choice of the mixed solvent, but there are at present no criteria for this selection (cf. Part I[1])—more experimentations must be done. Another way, based on phenomenological consider-ations, is to shift the working point closer to the critical point of the ternary system, since the interfacial tension vanishes at this point, because the phases become identical.

TABLE II

Preparative Fractionation of PIB II in the Mixed Solvent TOL/MEK

(a) Working parameters: $T = 25°C$

Step	u_2^{FD}	u_3^{FD}	u_2^{EA}	$\dot{V}^{FD}$ (cm³/min)	$\dot{q}$	$\dot{m}_3^{FD}$ (g/min)	A	ν	M_w^{FD} [a]	U^{FD} [a]	Remarks	Duration of experiment
I	0.170	0.150	0.250	4.93	5.3	0.637	5	3.5	98,400	1.4		2 × 26 h
II	0.169	0.148	0.225	3.95	6.3	0.503	5	3.5	137,000	0.70	GL from step I	32 h
IIIa	0.166	0.123	0.2175	4.00	6.3	0.422	5	4.0	195,000	0.50	GL from step II	16 h
IIIb	0.176	0.149	0.235	3.88	5.5	0.498	5	4.0	95,000	0.50	SL from step II	16 h

(b) Experimental results

Step	$\dot{V}^{GL}$ (cm³/min)	$\dot{V}^{SL}$ (cm³/min)	u_3^{GL}	u_3^{SL}	$\dot{m}_3^{GL}$ (g/min)	$\dot{m}_3^{SL}$ (g/min)	$\dot{m}_3^{GL} + \dot{m}_3^{SL}$ (g/min)	$\dot{G}$	M_w^{GL}	U^{GL}	M_w^{SL}	U^{SL}
I	1.64	29.4	0.218	0.0130	0.308	0.324	0.632	1.05	137,000	0.7	Rejected	—
II	1.72	27.1	0.170	0.0106	0.252	0.245	0.497	0.97	195,000	0.5	95,000	0.5
IIIa	1.66	27.6	0.1474	0.0092	0.211	0.217	0.428	1.03	256,000	0.30	168,000	0.29
IIIb	1.41	23.9	0.1963	0.0129	0.238	0.262	0.500	1.10	131,000	0.25	80,000	0.24

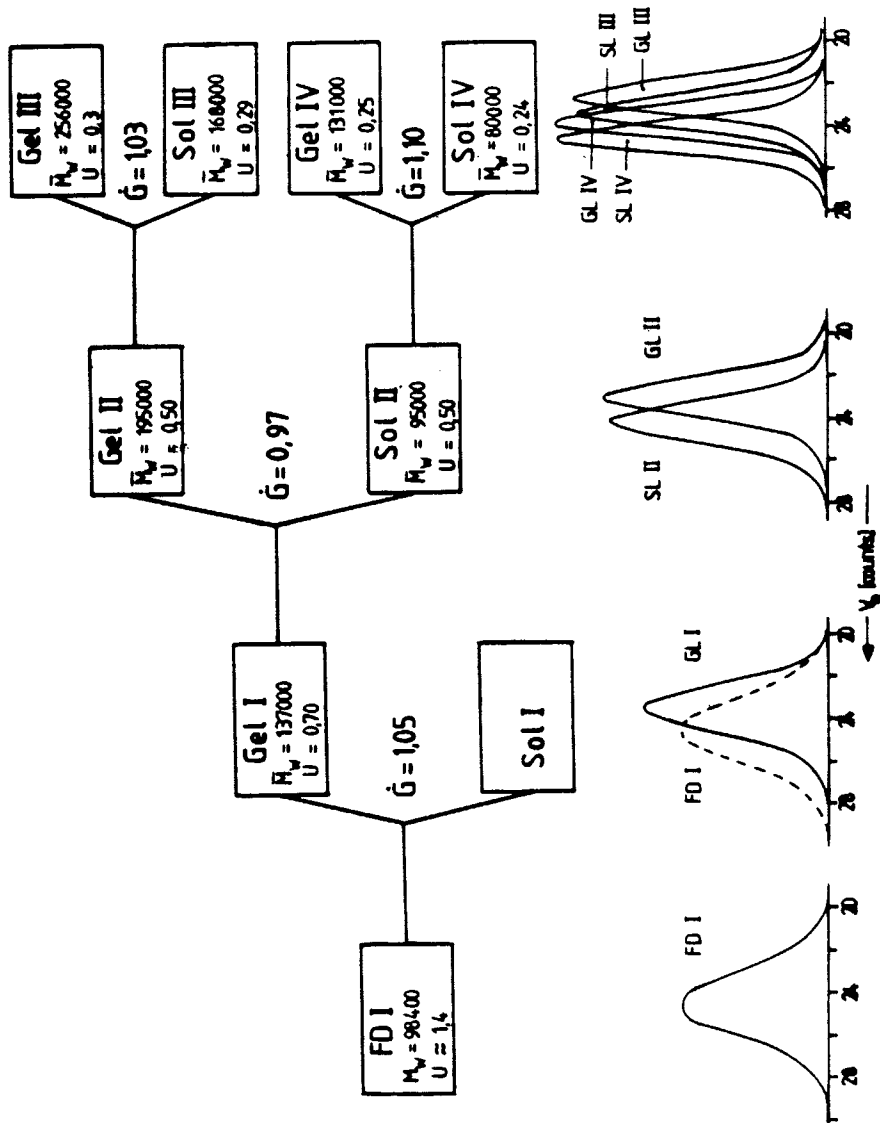[a] All M_w values and U values result from GPC measurements.

Fig. 7. Scheme of the fractionation procedure consisting of three CPF steps performed with PIB II using the mixed solvent toluene–methyl ethyl ketone. $\dot{G}$ = weight ratio of the polymer delivered per time unit in the sol-phase to that in the gel-phase; M_w = weight average molecular weight; U = nonuniformity $((M_w/M_n) - 1)$. The lower part of the figure shows the normalized GPC eluation curves for the starting material and for the different fractions.

CPF in the mixed solvent HEP / MEK

Because of the small differences in the densities of the components in the system TOL/MEK/PIB II, the mixed solvent had to be replaced by another solvent/nonsolvent pair.

Considering the quality of the equilibrium fractionations reported in Part I,[1] the following mixed solvents seem suitable: TOL/IPA, DBE/HEP, and HEP/MEK. From these the latter (ρ_{HEP} = 0.684 g/cm^3) was chosen for the experiments mentioned above.

In CPF runs with working points near the consolute point, the solvent quality of the extracting agent is good (w_2^{EA} is low), and relatively high $\dot{G}$ values result (cf. Fig. 5). Hence, in order to obtain $\dot{G}$ values of 1 or less, very small flow ratios $\dot{q}$ are necessary.

Variation of w_2^{EA}. In order to compare the separating effects in both mixed solvents, experiments were carried out using a constant flow ratio $\dot{q}$ of ca. 5. The weight fraction of the nonsolvent in the EA was varied between 0.5 and 0.6 giving $\dot{G}$ values between 0.3 and 2.8 (cf. Fig. 8).

The molecular weight of the polymer increases from 88,000 to 166,000 in the gel phases and from 30,000 to 62,000 in the sol phases with increasing $\dot{G}$ value (cf. Fig. 9). All experimental data and results are collected in Table III.

From Figure 9 one can interpolate the following values for M_{GPC} corresponding to $\dot{G} = 1$: M_{GPC}^{SL} = 43,000 and M_{GPC}^{GL} = 124,000. This is a slight improvement over the separation effect in the TOL/MEK system where M_{GPC}^{SL} = 46,000 and M_{GPC}^{GL} = 118,000.

In addition, the weight average molecular weights (M_w) and nonuniformities (U) of the polymers in the gel phases were determined from the GPC curves to be 114,000–193,000 and U = 0.63–0.46, respectively.
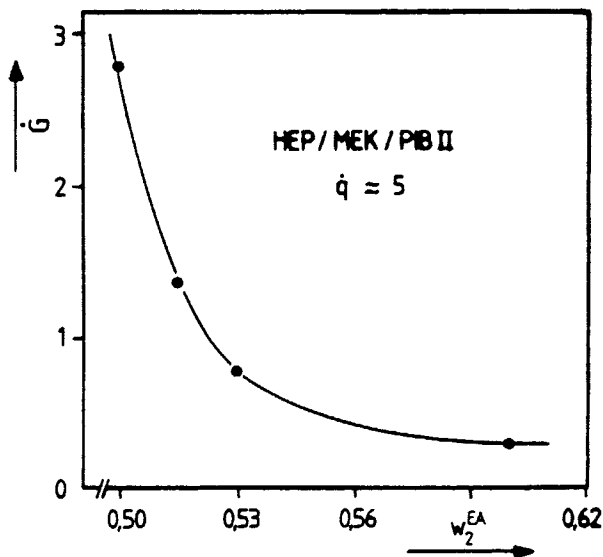

Fig. 8.   System HEP/MEK/PIB II: weight ratio $\dot{G}$ of the polymer leaving the column in the sol and in the gel, as a function of the weight fraction of nonsolvent in the extracting agent at the ratio of the flows entering the column of ca. $\dot{q}$ = 5 and a polymer concentration in the feed of 15 wt %.

TABLE III

Fractionation of PIB II in the Mixed Solvent HEP/MEK—Variation of u_2^{EA}

(a) Working parameters: $T = 25°C$

No.	u_2^{FD}	u_3^{FD}	u_2^{EA}	$\dot{V}^{FD}$ (cm³/min)	$\dot{q}$	$\dot{m}_3^{FD}$ (g/min)	A	ν	M_w^{FD}	M_{GPC}^{FD}	$b_{1/2}^{FD}$ (cm)	U^{FD}
6	0.38	0.150	0.50	5.00	5.6	0.567	10	3.5	98,400	73,200	3.50	1.4
7	0.38	0.150	0.515	4.91	5.06	0.557	10	3.5	98,400	73,200	3.50	1.4
8	0.38	0.150	0.53	4.60	6.1	0.521	10	5	98,400	73,200	3.50	1.4
9	0.38	0.150	0.60	4.39	6.3	0.498	10	5	98,400	73,200	3.50	1.4

(b) Experimental Results

| No.	$\dot{V}^{GL}$ (cm³/min)	$\dot{V}^{SL}$ (cm³/min)	u_3^{GL}	u_3^{SL}	$\dot{m}_3^{GL}$ (g/min)	$\dot{m}_3^{SL}$ (g/min)	$\dot{m}_3^{GL} + \dot{m}_3^{SL}$ (g/min)	$\dot{G}$	M_{GPC}^{GL}	$b_{1/2}^{SL}$ (cm)	M_w^{GL}	U^{GL}	M_w^{GL}	$b_{1/2}^{SL}$ (cm)
6	0.85	33.0	0.2274	0.0165	0.147	0.409	0.556	2.78	166,000	2.89	189,000	0.46	62,000	2.35
7	1.36	28.4	0.2343	0.0156	0.241	0.328	0.569	1.36	124,000	2.56	146,000	0.52	45,000	2.54
8	1.43	31.3	0.2650	0.0096	0.287	0.223	0.510	0.78	106,000	2.47	133,000	0.65	39,000	2.83
9	1.79	30.2	0.2851	0.0052	0.385	0.117	0.502	0.304	88,000	2.27	114,000	0.68	31,000	3.10
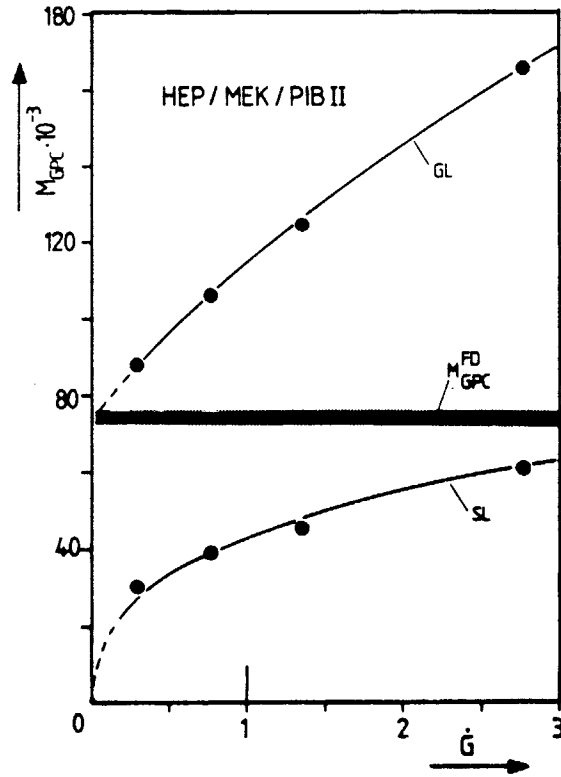
Fig. 9. System HEP/MEK/PIB II: molecular weights M_{GPC} (maximum of the GPC eluation curve) of the polymers leaving the column in the sol and in the gel as a function of the weight ratio $\dot{G} = \dot{m}_3^{SL}/\dot{m}_3^{GL}$. For comparison M_{GPC} of the starting material PIB II is indicated by the shaded band.

Variation of $\dot{q}$ at different values of w_2^{EA}

The CPF experiments with working points closer to the consolute point were started with an extracting agent containing 50 wt % nonsolvent. As in all other experiments, a feed with $w_3 = 0,15$ and a flow of ca. 5 cm^3/min ($\rightarrow \dot{m}_3^{FD} \approx 0.5$–$0.6$ g/min) was chosen where the flow ratios $\dot{q}$ ranged between 1.4 and 5.6.

Because of the relatively low content of the nonsolvent in the EA, only $\dot{G}$ values greater than 1.6 could be realized. This corresponds to a maximum of 40% of the original polymer leaving the column in the gel phase. Therefore, in the next CPF run, the concentration of MEK in the EA was increased from 50 to 51.5 wt %; $\dot{q}$ was then varied over a greater range of 0.85–8. With the resulting working points, it was possible to attain $\dot{G}$ values smaller than 1.

The complete working parameters and results of these runs are summarized in Table IV. Figure 10 shows the phase diagram of the system HEP/MEK/PIB II as well as the two working lines and corresponding working points, i.e., average composition of the total content in the column under stationary operating conditions.

Before discussing the differences in the separation effects between the two sets of runs of different w_2^{EA}, it should be noted that these experiments were

TABLE IV

Fractionation of PIB II in the Mixed solvent HEP/MEK—Variation of $\dot{q}$

(a) Working parameters: $T = 25°C$

No.	u_2^{FD}	u_3^{FD}	$\dot{V}^{SL}$ (cm³/min)	u_2^{EA}	u_3^{SL}	$\dot{V}^{FD}$ (cm³/min)	$\dot{q}$	$\dot{m}_3^{FD}$ (g/min)	A	ν	M_w^{FD}	M_{GPC}^{FD}	$b_{1/2}^{FD}$ (cm)	U^{FD}
10	0.38	0.150	10.8	0.50	0.0443	5.08	1.4	0.579	8	3.59	98,400	73,200	3.50	1.4
11	0.38	0.150	19.3	0.50	0.0263	4.98	3.0	0.564	8	3.5	98,400	73,200	3.50	1.4
12 = 6	0.38	0.150	33.0	0.50	0.0165	5.00	5.6	0.567	10	3.5	98,400	73,200	3.50	1.4
13	0.38	0.150	7.6	0.515	0.0418	5.06	0.85	0.574	8	3.5	98,400	73,200	3.50	1.4
14	0.38	0.150	17.3	0.515	0.0241	5.00	2.76	0.567	8	3.5	98,400	73,200	3.50	1.4
15	0.38	0.150	28.4	0.515	0.0156	4.91	5.06	0.557	10	3.5	98,400	73,200	3.50	1.4
16	0.38	0.150	44.1	0.515	0.0111	5.03	8.0	0.571	10	3.5	98,400	73,200	3.50	1.4

(b) Experimental results

| No.	$\dot{V}^{GL}$ (cm³/min)	$\dot{V}^{SL}$ (cm³/min)	u_3^{GL}	u_3^{SL}	$\dot{m}_3^{GL}$ (g/min)	$\dot{m}_3^{SL}$ (g/min)	$\dot{m}_3^{GL} + \dot{m}_3^{SL}$ (g/min)	$\dot{G}$	M_{GPC}^{GL}	$b_{1/2}^{GL}$ (cm)	M_w^{GL}	U^{GL}	M_{GPC}^{SL}	$b_{1/2}^{SL}$ (cm)
10	1.32	10.8	0.2244	0.0443	0.224	0.357	0.581	1.59	139,000	2.62	168,000	0.52	55,000	2.62
11	1.01	19.3	0.2230	0.0263	0.171	0.382	0.553	2.23	156,000	2.40	182,000	0.46	58,600	3.02
12 = 6	0.85	33.0	0.2274	0.0165	0.147	0.409	0.556	2.78	166,000	2.27	189,000	0.46	61,600	3.10
13	1.81	7.6	0.2300	0.0418	0.316	0.236	0.552	0.75	104,000	2.94	127,000	0.69	39,500	2.75
14	1.55	17.3	0.2323	0.0241	0.272	0.308	0.580	1.13	120,000	2.60	140,000	0.56	44,000	2.81
15	1.36	28.4	0.2343	0.0156	0.241	0.328	0.569	1.36	124,000	2.47	146,000	0.52	45,500	2.83
16	1.18	44.1	0.2379	0.0111	0.213	0.363	0.576	1.70	136,000	2.32	157,000	0.51	51,500	2.86
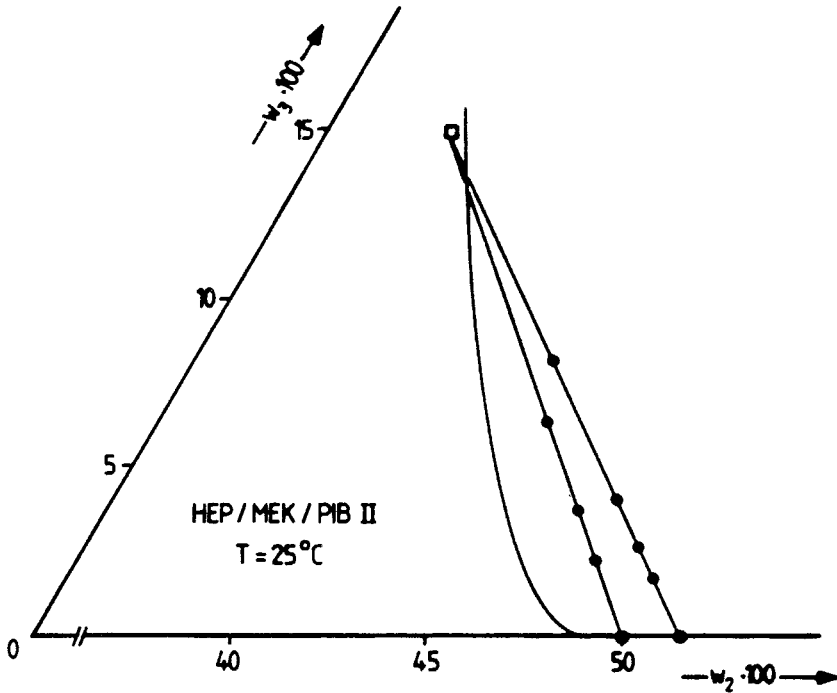
Fig. 10. Phase diagram of the system n-heptane/methyl ethyl ketone/PIB II at 25°C and working lines of the experiments collected in Table IV: w_i = weight fraction of component i; (□) feed; (●) extracting agent; (·) working point.
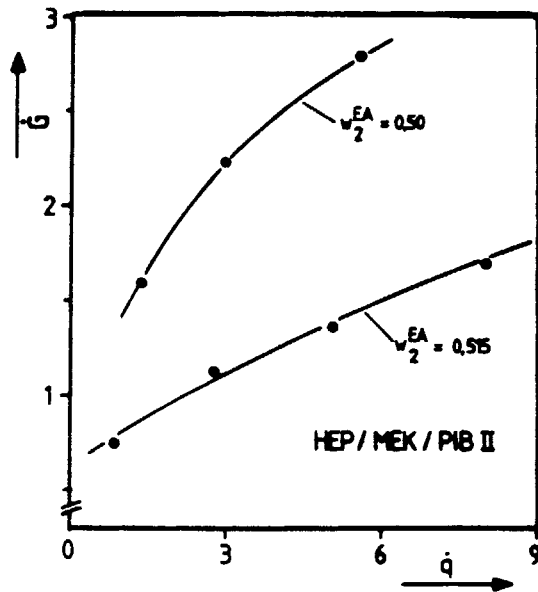

Fig. 11. System HEP/MEK/PIB II: weight ratio $\dot{G}$ of the polymer leaving the column in the sol and in the gel, respectively, as a function of the ratio $\dot{q}$ of the flows entering the column at the two indicated values of w_2^{EA}.

conducted without any problems even in the range of small $\dot{q}$ values. The visual appearance in the column was the same as in all other experiments, except that the average diameter of the gel droplets was smaller, in the experiments performed closer to the consolute point. The measured mass balances (cf. Table IV) show that even at high polymer concentration in the separating column (max. 6.5 wt %) a stationary state can be reached.

In Figure 11, $\dot{G}$, the ratio of the mass fluxes, is plotted as a function of the flow ratio $\dot{q}$ entering the column. As expected, both curves have a positive slope, but that of $w_2^{EA} = 0.5$ is steeper than that of $w_2^{EA} = 0.515$. The effect of $\dot{q}$ on $\dot{G}$ increases as the working line is moved closer to the consolute point in agreement with the fractionation of PVC.[6]

Finally, Figure 12 shows the molecular weights (M_{GPC}) of the polymer in either phase as a function of $\dot{G}$. In Figure 13 the weight average molecular weight was plotted rather than M_{GPC}, because M_w gives a more accurate representation of the separation effect. As mentioned in the footnote of the first section, it is not possible to calculate M_w^{SL} from the GPC curve for the present case. Therefore, the molecular weights (M_w^{SL}), contained in Figure 13, were determined according to eq. (3), using the experimental M_w^{FD}, M_w^{GL}, and $\dot{G}$ values.
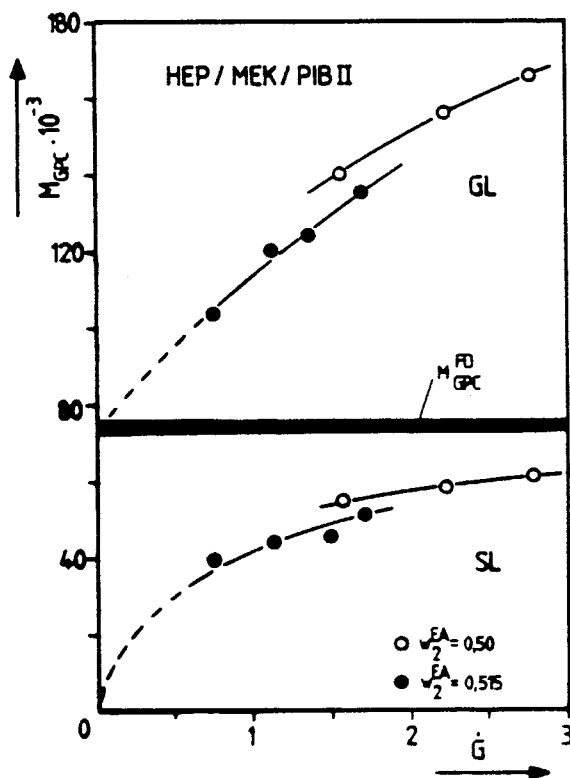

Fig. 12. System HEP/MEK/PIB II: molecular weights M_{GPC} (maximum of the GPC eluation curve) of the polymers leaving the column in the sol and in the gel as a function of the weight ratio $\dot{G} = \dot{m}_3^{SL}/\dot{m}_3^{GL}$ at the two indicated values of w_2^{EA}. For comparison M_{GPC} of the starting material PIB II is indicated by the shaded band: (○) $w_2^{EA} = 0.50$; (●) $w_2^{EA} = 0.515$.
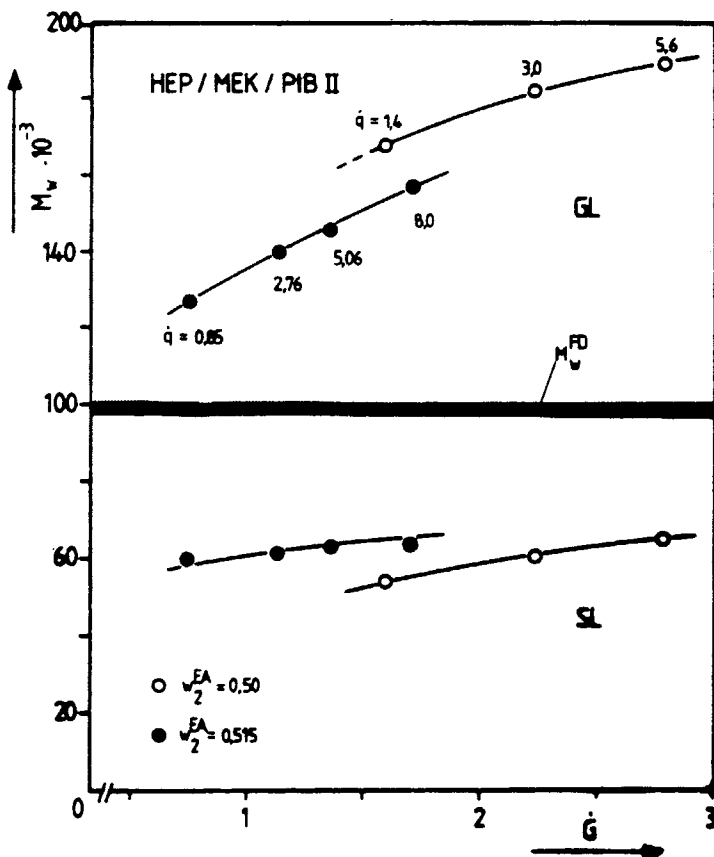
Fig. 13.   System HEP/MEK/PIB II: molecular weights M_w (weight average) of the polymers leaving the column in the sol and in the gel as a function of the weight ratio $\dot{G} = \dot{m}_3^{SL}/\dot{m}_3^{GL}$ at the two indicated values of w_2^{EA}. M^{SL} values are calculated according to eq. (3). For comparison M_w of the starting material PIB II is indicated by the shaded band: (○) $w_2^{EA} = 0.50$; (●) $w_2^{EA} = 0.515$.

Although the $\dot{G}$ values of both CPF runs overlap only in a small region, the results indicate in a clear manner that there is a better separation effect in the runs with $w_2^{EA} = 0.50$. For example, at $\dot{G} = 1.5$ the differences of the molecular weights of the polymer in the coexisting phases ($\Delta M_w = M_w^{GL} - M_w^{SL}$) are 110,000 for $w_2^{EA} = 0.50$, but only about 85,000 for $w_2^{EA} = 0.515$. Normally the fractionation quality decreases with increasing polymer concentration,[7-9] but with the present results one observes the opposite effect. This is because the working point of the run with the higher polymer concentration lies closer to the consolute point, and is therefore associated with a higher degree of dispersion and consequently better separation.

CONCLUSION

Using a relatively low molecular weight PIB sample ($M_w = 98,400$), it was studied how the subdivision of the original polymer sample into the coexisting phases (as measured by $\dot{G}$), as well as the separation quality (as measured by ΔM) are influenced by the choice of the working parameters. An increase in

the $\dot{G}$ values can be reached in two ways: first by decreasing the weight fraction of nonsolvent in the extracting agent ($\dot{q}$ = const) and second by increasing the flow ratio $\dot{q}$ (w_2^{EA} = const). The results show that the influence of w_2^{EA} on $\dot{G}$ is stronger than that of $\dot{q}$, especially if the working line lies very far inside the miscibility gap.

If the density of the mixed solvent is sufficiently lower than that of the polymer, the CPF can be made to operate in the vicinity of the consolute point of the ternary system. The advantage of this mode of operation is the decrease of interfacial tension between the coexisting phases, which leads to a better dispersion of the gel droplets and to better mass transfer. But now $\dot{q}$ ratios as low as 1 are needed to get $\dot{G}$ values of 1 or smaller. This leads to unusually high polymer concentrations in the column. However, the decrease of the separation quality due to the polymer concentration effect is compensated for by the better mass transfer. This method of operation affords an enormous saving of the low molecular weight liquids: per minute it is possible to fractionate at maximum 1 g polymer using only 10 cm^3 solvent/nonsolvent.

Concerning the choice of the best suited mixed solvent, the most important point lies in a good separation effect (large ΔM) as observed in equilibrium experiments; furthermore, the difference in the densities of EA and the pure polymer should be large in order to be able to perform experiments close to the consolute point of the ternary system.

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