Level and Kinetics of PVP Extraction from Blends, Interpenetrating Polymer Blends, and Semiinterpenetrating Polymer Networks

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ABSTRACT: Extraction level and kinetics are key parameters that control the properties of materials made of polymer blends when they are in contact with a liquid medium. Poly(vinylpyrrolidone) (PVP)–poly(methacrylate) polymer blends (PBs), interpenetrating polymer blends (IPBs), and semiinterpenetrating polymer networks (s-IPNs) were synthesized in the film form by a UV curing process (except in PBs cases). The extent of PVP extraction from these materials by water was investigated by monitoring the PVP content in the extracting medium. PVP was generally well extracted from PBs and from IPBs, but only partially from s-IPNs and one IPB. The strong limitation of PVP extraction in the last cases was attributed to the high cross-linking density of the matrices. It can be explained by a blocking of the reptation linear chains by nooses around branches of the network. The diffusion coefficient of PVP in these materials, which was calculated by fitting kinetics data with a solution of second Fick's law, depends strongly on the network chemical nature and PVP content in the poly(methacrylate) matrix. Extraction of a polymer from s-IPN could then be prevented by choosing properly the composition of the blend and the nature of the poly(methacrylate) component.

Introduction

The wide range of morphological characteristics and physical properties obtainable by blending polymers of various chemical natures has generated increasing interest in understanding the relationship between structure and property. The ultimate goal of such understanding is obviously to optimize the blend materials to meet specific applications. Most published works concern the miscibility of blend components[1–5] and the physical properties of the blends in the dry form, with special attention to the thermomechanical properties.[6–8] However, blend materials may come into contact, accidentally or purposely (hoses, tanks, pipelines, etc.), with a liquid medium in their use. In some special applications, such as membranes for separation processes, blends are required to work in contact with a liquid medium. In such cases, one component of a blend can be extracted out of the materials into the liquid medium if the component is soluble in the liquid. As the extraction leads to changes in the composition and morphological characteristics of blends, the extractability of a soluble polymer component as well as its extraction kinetics are key parameters for properly using the material.

There are two limiting cases which seem to be simple according to common knowledge. On one hand, if the polymer components are incompatible, there would be complete extraction of the soluble component by the liquid medium. On the other hand, block copolymers or polymer blends in which the polymer components are covalently linked together or physically bound by strong electrostatic interactions must show no extraction of the soluble component, even if the components are incompatible. The situation is more complex in the case of completely miscible polymer blends and the question of whether the chain entanglements and weak physicochemical bonds between polymer components may limit the extraction, and to which extent, remains open. The only studies on blends of completely miscible blends have been done in atypical situations. Mark and Zhang[9] showed that soluble poly(dimethylsiloxane) chains can be quasicompletely extracted out of a cross-linked network of the same polymer. However, this case involved short chains of the linear component and a largely swollen host polymer matrix. Meyer et al.[10] reported a partial retention of the poly(styrene-*co*-isoprene-*co*-styrene) trapped in a polystyrene cross-linked network in extraction experiments but did not examine the retention mechanism.

The aim of the present study was to analyze the efficiency and the kinetics of extraction of a soluble linear polymer trapped in a polymer matrix of a different chemical nature. We chose poly(*N*-vinylpyrrolidone) (PVP) as the model soluble linear polymer because it is commercially available in a broad range of molecular weights and because it is easily quantified in the extracting medium.[11,12] The medium chosen was water. The polymer matrices we used had been obtained by photopolymerization of methacrylate derivatives to lead to un-cross-linked or cross-linked matrices. The polymerization reaction was performed on solutions containing PVP and monomers, so that the obtained blends were of the following types: interpenetrating polymer blends (IPBs), or semiinterpenetrating polymer networks (s-IPNs). In the latter type, one polymer is cross-linked, restricting the chain mobility and therefore limiting the reorganization into individual rich phase. By comparing the extraction efficiency and kinetics of systems of different chain interpenetration degrees, we expect to obtain the influence of the structure of the host material on the behavior of the linear polymer. Furthermore, we studied the influence of the chemical nature of the host network in which the linear polymer is trapped by using films photochemically obtained with mono- or bifunc-

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tional monomers of different natures in various proportions.

With this investigation, we expect to improve our understanding of the extraction of a polymer trapped in a network of another polymer. This understanding is of particular importance in the area of polymer materials for membrane processes in which we are involved: polymer blends can be used in pervaporation for solvent fractionation;[13] they are also used in the manufacture of asymmetric hollow fibers for ultrafiltration.[14]

Background

Extraction Efficiencies. When the polymer component is soluble in the extracting liquid, its extraction can be very efficient, provided that the extracting liquid is renewed so as to keep the polymer concentration at a very low level. The extraction rate decreases with time because the extraction driving force decreases. However, as unattached chains would move through the nonsoluble network of polymer according to a "reptation" mechanism,[15,16] there is virtually no obstacle to their total extraction. The polymer extraction is therefore theoretically complete at infinite time. Experimental results on the extraction of unattached poly(dimethylsiloxane) in a network of cross-linked chains of the same chemical nature[9] support this prediction. Only cyclic polymers large enough to be threaded through by growing chains of a cross-linked network could be trapped to a certain extent.[17]

Extraction Kinetics. The mass center diffusion of a polymer chain of molecular weight M in an entangled network may take place according to three different processes: reptation,[15,16] Stokes–Einstein diffusion,[18,19] and constraint release.[18–21] The last process results from the release by diffusion of the constraints set by the neighboring matrix chains on the tube in which the considered linear polymer chain crawls.

The reptation theory[15,16] predicts that the diffusion coefficient of a chain in a polymer matrix occurs by reptation in a tubelike region defined by the topological constraints of the neighboring chains. The diffusion coefficient of an individual chain in this case depends on its molecular weight[22] as M^{-2}.

The collective motion (Stokes–Einstein diffusion) of chains, which is associated with the relaxation of concentration fluctuations (against the viscous friction of the surrounding medium), would be negligible in this case.

The reptation model was developed for the self-diffusion in semidilute polymer solutions. No model is available for the diffusion of a polymer in the matrix of another polymer. The role of the interaction between different monomer units remains undescribed.

If we assume that the motion of an unattached chain in a chemically different polymer matrix is characterized by a mean diffusion coefficient whatever its diffusion mechanism, its extraction kinetics could be described by eq 1:[32]

$$\frac{C_f - C_t}{C_f - C_0} = \frac{8}{\pi^2}\sum_{\nu=0}^{n}\frac{1}{(2\nu + 1)^2}\exp\left[-(2\nu + 1)^2\frac{\pi^2 Dt}{l^2}\right] \quad (1)$$

Where C_f = concentration of the solute in the slab at time $t = \infty$, C_0 = concentration of the solute in the slab at time $t = 0$, C_t = concentration of the solute in the slab at time t, l = slab thickness, t = time, and D = average diffusion coefficient for the solute diffusion into or out a semiinfinite slab. Using mass balance between the membrane slab and the extracting medium, we can derive a similar equation for the concentration of extracted species in solutions (which is effectively determined):

$$\frac{C'_f - C'_t}{C'_f} = \frac{8}{\pi^2}\sum_{\nu=0}^{n}\frac{1}{(2\nu + 1)^2}\exp\left[-(2\nu + 1)^2\frac{\pi^2 Dt}{l^2}\right] \quad (2)$$

Where C'_f = concentration of the solute in the extracting medium at time $t = \infty$, C'_0 = concentration of the solute in the extracting medium at time $t = 0$, C'_t = concentration of the solute in the extracting medium at time t, and D = average diffusion coefficient for the solute diffusion into or out a semiinfinite slab.

In principle, we must take into account the diffusion of the extracting solvent into the polymer slab; without the presence of solvent molecules at a point in the membrane, there is no driving force for the diffusion of the extractable component. However, the problem of simultaneous diffusion of solvent (in) and polymer (out) in the slab in very complex. We simplify it by considering the solvent diffusion much more rapid than the polymer diffusion and assume its influence on the polymer extraction kinetics negligible. We will use the mean diffusion coefficient obtained from the described procedure as an overall parameter to characterize the extraction kinetics without looking into the detailed diffusion mechanism.

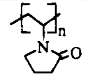
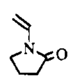
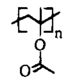
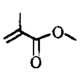
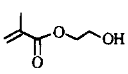
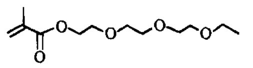
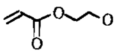
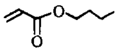
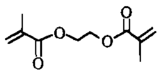
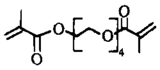
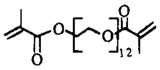
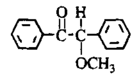
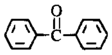
Experimental Section

Dense Film Synthesis. Chemicals. The basic products used in this study were the following: poly(vinylpyrrolidone) (PVP) of different average molecular weights (respectively 40 000, 160 000, and 360 000), purchased from Fluka, medium average weight poly(methylmethacrylate) (PMMA) from Aldrich, and methacrylic monomers and methyl ether benzoin (photoinitiator) from Polysciences. All these products, described in Table 1, were used without further purification. PVP–PMMA blend membranes were made by first dissolving PVP and PMMA in chloroform, then casting the solution onto a polycarbonate plate, and finally completely evaporating the solvent.

Interpenetrating polymer networks (or blends) with PVP were prepared according to the following procedure: PVP and methacrylic monomers were dissolved in ethanol to obtain a 10 wt % PVP solution. Then dissolved gases were removed by three cycles (freezing of the polymer flask in liquid air, vacuuming, warming up under static vacuum, returning to atmospheric pressure by nitrogen injection). After this treatment, the photoinitiator was added (3 mol % per mole of photopolymerizable function present in solution), and the obtained dope was thoroughly mixed and quickly cast onto a polycarbonate support film. The last step consisted of an ultraviolet (UV) curing at 365 nm in a nitrogen atmosphere. The reaction can also be monitored at 815 cm^{-1} by an infrared (IR) spectrophotometer equipped with an attenuated total reflectance (ATR) device. In this case, the formulation was cast directly onto the ATR crystal instead of a polycarbonate support film.

After 12 h under UV light, all the monomer molecules were generally converted into polymers. The membranes obtained were ca. 40 μm thick. The following nomenclature will be used for the obtained membranes: for PVP–polymer blends, PVP$_{\text{average molecular weight}}$–POLYMER mole unit % of PVP–mole unit % of polymer (example:PVP$_{360000}$–PMMA 75–25 stands for a blend of PVP of molecular weight 360 000 with PMMA in a mole unit ratio 75% vinylpyrrolidone (VP)/25% MMA) and for PVP–polymethacrylate IPBs or IPNs, PVP$_{\text{average molecular weight}}$–MONOMER mole unit % of PVP–mole % of monomer (example: PVP$_{360000}$–EGDMA 75–25 stands for the interpen-

Table 1. Products Used, Their Name, Formula, and Abbreviation

Compound name	developed formula	symbol used
poly(vinylpyrrolidone)		PVP
vinylpyrrolidone		VP
poly(methylmethacrylate)		PMMA
methylmethacrylate		MMA
2-hydroxy ethyl methacrylate		HEMA
2-(2,2-ethoxyethoxyethoxy ethyl methacrylate)		TEEMA
2-methoxy ethyl acrylate		MEA
n-butyl acrylate		nBuA
ethyleneglycol dimethacrylate		EGDMA
polyethyleneglycol 200 dimethacrylate		PEG200DMA
polyethyleneglycol 600 dimethacrylate		PEG600DMA
methyl ether benzoin		
benzophenone		

etrating network made of PVP of molecular weight 360 000 trapped in UV-cured EGDMA (ethylene glycol dimethacrylate) in a mole ratio 75% VP unit/25% EGDMA).

Extraction Procedure. A series of 10 identical samples was extracted in identical volumes of water (50 cm^3) at 60 °C and the PVP concentration in the extracting media was successively determined at different extraction times.

PVP Analysis Procedure. In aqueous media PVP reacts with the Lugol reagent (I_2–I^- mixture) leading to a characteristic red color.[11] Under controlled conditions (pH, temperature, reagent concentration), extracted PVP can be quantitatively determined by UV spectrophotometry (e.g. at 400 nm) of the soluble PVP–iodine–iodide complex.

The Lugol reagent was prepared according to Neel and Sebille's procedure:[12] 1 g of I_2 and 2 g of KI are dissolved in 300 cm^3 of distilled water; 15 cm^3 of this solution is diluted to 1000 cm^3 with acetic buffer (pH = 4.75) to obtained fresh Lugol standard reagent. Lugol reagent (3.0 cm^3) was added to 1.0 cm^3 of PVP aqueous solution to be analyzed. A reference solution was made by using 1.0 cm^3 of distilled water with 3.0 cm^3 of Lugol reagent. The calibration curve was obtained by measuring the 400 nm absorbance, in a Philips PU 8730 spectrophotometer, of PVP_{360000}–iodure solutions of different concentrations.

To know whether the PVP molecular weight may affect the analysis results, three solutions containing 120 mg/L of respectively PVP_{40000}, PVP_{160000}, and PVP_{360000} were analyzed according to the above-given procedure. The results indicated that the extinction coefficient of the complex does not depend on the PVP molecular weight.

Results and Discussion

PVP Extraction Rate from Blend Materials. When two polymers are mixed, the resulting material is a polymer blend (BP), but when a polymer is first mixed with a methacrylate monomer and then polymerized, the final material is an interpenetrating polymer blend (IPB). The difference between the two materials lays in the interpenetration degree which is higher for IPB than for PB because of the good dispersion of the monomer, including inside the polymer coils. Our first interest is to study the influence of the degree of interpenetration with the nonsoluble polymer component on PVP extraction for PVP-based blends. Secondly we are interested in the possible blocking effect of the nonsoluble polymer on PVP extraction.

Table 2. Twenty-Four Hour Extraction of Some PVP Polymer Blends and PVP Interpenetrating Polymer Blends by Stirred Distilled Water at 60 °C[a]

formulation used	PVP extracted fraction (%)	$D_{PVP} \times 10^9$ (cm^2/s)
PVP_{360000}	100	very high
PVP_{360000}–PMMA 75–25 (blend)	100	18.2
PVP_{360000}–MMA 75–25	100	5.0
PVP_{360000}–MMA 50–50	100	2.4
PVP_{360000}–HEMA 75–25	95.5	7.0
PVP_{360000}–HEMA 50–50	91.1	5.5
PVP_{360000}–TEEMA 90–10	90.4	3.0
PVP_{360000}–TEEMA 75–25	26.0	1.3
PVP_{360000}–TEEMA 50–50[b]	44.0	5.0

[a] PVP extracted fractions and diffusion coefficients D_{PVP} obtained by fitting with eq 2. [b] Phase separated material.

Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2-(2-ethoxy-2-ethoxyethoxy)ethyl methacrylate (TEEMA), and poly(methyl methacrylate) (PMMA) were used as the monomers for the nonsoluble polymer component of the IPB. The PVP extraction ratio and the diffusion coefficient of PVP through the nonsoluble polymer material are shown in Table 2.

The rate of dissolution for the pure PVP film in water was much faster than the rate of PVP extraction from any blend materials. This can be explained by the fact that, in the extraction of PVP from any blends with a nonsoluble component, the rate-limiting step is the diffusion of PVP chains through the nonsoluble polymer, whereas in the dissolution of PVP by a solvent under stirring, it is probably the diffusion of solubilized PVP chains through the stagnant boundary layer in the vicinity of polymer particles. Indeed, since PVP, on one hand, was extracted from the blends at the same rate whatever the stirring speed, provided that the latter was not too low, we concluded that the mass transport in the liquid phase is not the rate-determining step. On the other hand, we can infer from the fact that the PVP extraction rates obeyed eq 2 (Figure 1), that the diffusion of PVP chains in the solid material controls the PVP extraction into the liquid.

The effect of the interpenetration degree can be seen from the comparison of the results obtained with PVP–PMMA 75–25 blend and PVP–MMA 75–25 interpenetrating polymer blend (Table 2). The higher diffusion coefficient of PVP chains in the PVP–PMMA blend material compared with that in the material made by polymerizing the methacrylate monomer in the semidilute PVP solution indicates (Figure 1) that PVP chains were more hindered in their reptation movement in the latter material. As the PMMA chains in this material were formed by addition to the living chains of methacrylate molecules which solvate PVP coils, PVP chains would be more intimately intermingled with PMMA chains than in blends of the two polymer species. The higher number of entanglement points of PVP chains

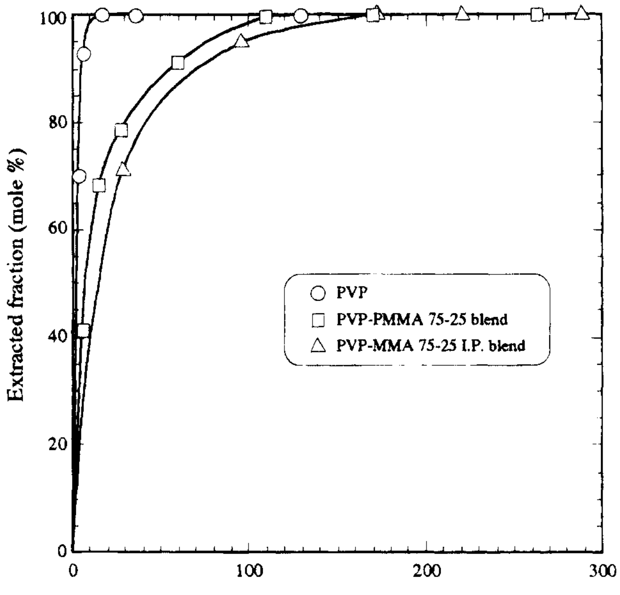


Figure 1. PVP extraction kinetics of PVP–PMMA blend and PVP–PMMA IPB: experimental points and best-fit curves (eq 2 with D values from Table 2).

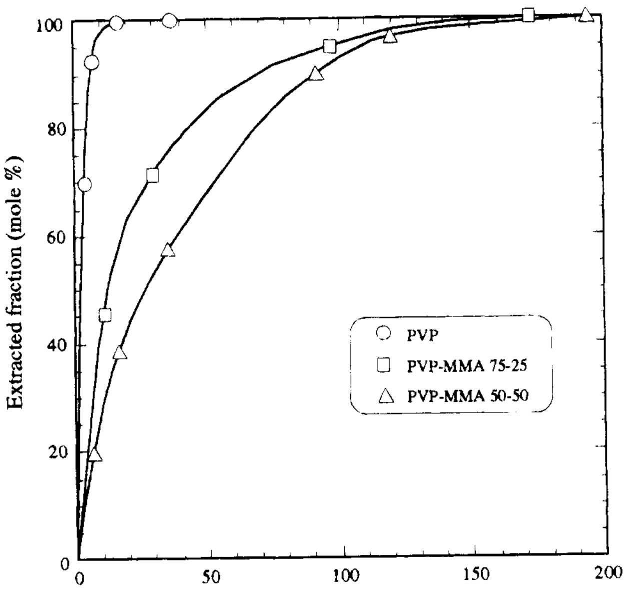


Figure 2. PVP extraction kinetics of PVP–MMA IPBs with different PVP/MMA ratios: experimental points and best-fit curves (eq 2 with D values from Table 2).

with the interpenetrated PMMA chains would be the cause of the hindered reptation of the PVP chains.

When we examined the extractability and the extraction rate of PVP chains in interpenetrated blends with methacrylate derivatives in different proportions, we observed a clear influence of the poly(methacrylate) nature and content on the two characteristics of the PVP extraction. For a series of materials with the same methacrylate derivative, the PVP diffusion coefficient decreases with increasing methacrylate contents (FIgure 2). Such behavior is consistent with the explanation based on the entanglement extent: the higher the content of nonsoluble polymer, the higher the number of entanglement points with the nonsoluble chains and the stronger the hindrance of the PVP reptation movement. For all PVP–PMMA blends and IPBs, the extracted fraction increases up to 100% at a rate well described by the model, as one can expect from the total solubility of PVP in water. Referring to these results, we can estimate that the strong decrease in the PVP extractability with the TEEMA content in the IPB appears to be singular. Indeed, in the frame of the reptation model, an unattached chain should be extractable by the solvent as long as the extraction driving force exists; the only difference should be the diffusion rate which depends on the entanglement extent and possibly on the cross-interactions between the polymer components. The fact that PVP extraction was strongly limited in some cases whereas the diffusion coefficient did not change very significantly with the change in the nature of the methacrylate component suggests that other phenomena may occur in the course of extraction.

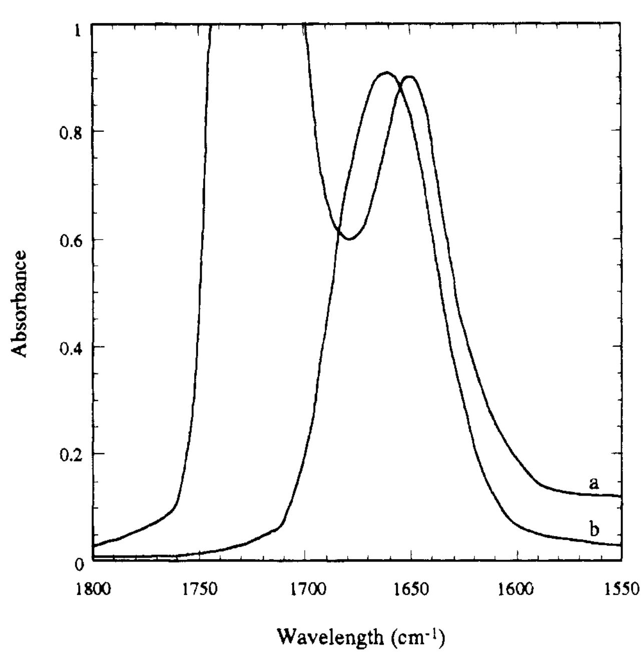


Figure 3. Infrared spectra of PVP (b) and PVP–HEMA 50–50 IPB (a) in the carbonyl absorption range.

Let us discuss in more detail the cases of the interpenetrating blend of PVP with poly(2-hydroxyethyl methacrylate) (HEMA case) and that with poly(2-(2-ethoxy-2-ethoxyethoxy)ethyl methacrylate) (TEEMA case).

HEMA Interpenetrating Blend. In this type of material, hydroxyl groups on lateral chains in poly(HEMA) must be involved in strong hydrogen bonding with carbonyl groups of PVP lateral chains in much the same way as that in poly(vinyl alcohol)–PVP blends.[23,24] Such strong interactions are evidenced by the shift of the C=O vibration frequency of PVP toward lower values in blends (Figure 3).

The extraction kinetics shown in Figure 4 indicate that in spite of the strong interactions between the blend components, the PVP extraction rate from these blends remains very high. However, part of PVP chains seems to exhibit slower mobility: contrary to the case of PVP interpenetrated by PMMA, for which normal extraction kinetics were observed (Figures 1 and 2), the PVP extracted fraction did not increase with time to 100% according to the kinetic model. Assuming that a finite fraction of PVP chains has a high diffusivity, the fitting of the fast increase in the extracted fraction with time (early part of the curve) by eq 2 makes it possible to estimate the values of this fraction. They are respectively 84% and 65% for the PVP–HEMA 75–25 and

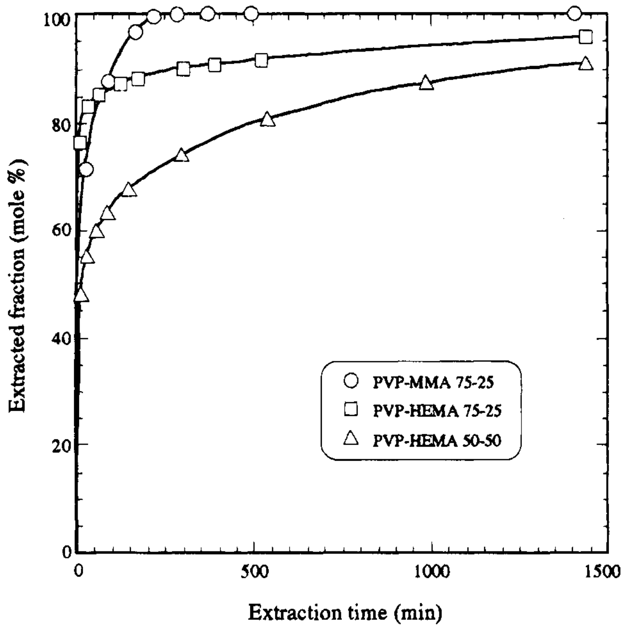


Figure 4. PVP extraction kinetics of PVP–HEMA IPBs with different PVP/HEMA ratios compared to PVP–MMA 75–25.

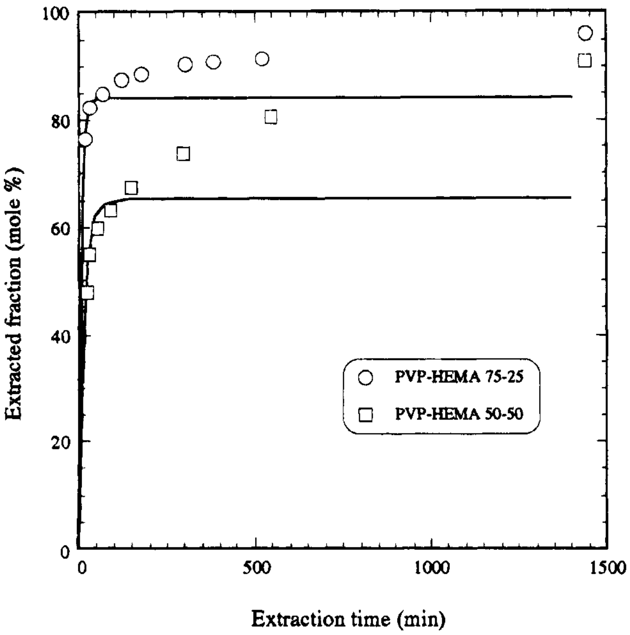


Figure 5. PVP extraction kinetics of PVP–HEMA IPBs with different PVP/HEMA ratios obtained by assuming that a PVP fraction has high extraction kinetics corresponding to the early parts: experimental points and best-fit curves (eq 2 with D values for Table 2).

50–50 films. The remaining PVP chains were then slowly extracted in a second step, as evidenced by the slow increase in the extracted fraction with time in the late part of the kinetics. The relevant experimental features can be seen in Figure 5: the initial PVP extraction rate is higher for the PVP–HEMA 75–25 system in the initial period than for the PVP–MMA 75–25 but it tends to level off for PVP–HEMA (at ca. 84% of extracted PVP), instead of increasing up to 100% as in the case of PVP–MMA. We speculate that the hydrogen-bonding interactions between HEMA and pyrrolidone moieties impede the reptation movement of a fraction of the PVP chains. The total interaction power would depend on the topological arrangement of the chains of the two species: for part of the PVP chains, the appropriate arrangement would make possible strong interactions between the two components which lead to slower diffusion. Nevertheless, as hydrogen bonds between the polymer components can be broken down and replaced by hydrogen bonds between polymer hydrophilic sites and water molecules, no permanent blocking effect of PVP is observed (Figure 4). Similar observations were made when polystyrene sulfonic acid was extracted from its blend with poly(vinyl alcohol).[25]

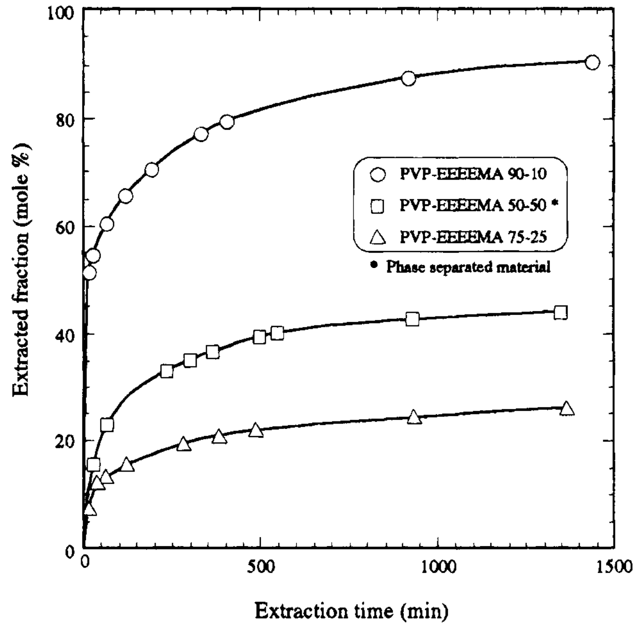


Figure 6. PVP extraction kinetics of PVP–TEEMA IPBs with different PVP/TEEMA ratios.

TEEMA Interpenetrating Blends. Figure 6 shows that the PVP extracted fractions from PVP–TEEMA systems are much lower than those from PVP–MMA and PVP–HEMA systems. The values of an extracted fraction after 24 h change with the TEEMA content: they are respectively 90%, 26%, and 44% for the IPB containing 10%, 25%, and 50% poly(TEEMA) (Table 2). The PVP extractability was strongly reduced when the TEEMA content increased. The reversal of the PVP extractability when TEEMA content is increased from 25% to 50% can be explained by a phase separation (opaque film) visible in the blend containing 50% TEEMA, whereas there is apparently no phase separation in systems containing less poly(TEEMA). The fact that the extracted fraction for the equimolar blend did not reach 100% as in the cases reported previously suggests that PVP was in the miscible phase with some amount of poly(TEEMA) rather than in a separate pure phase. DSC study of this blend confirmed our suggestion. Indeed, two T_g values were found for the phase-separated material (50% TEEMA); one T_g value (−50 °C) corresponds practically to that for pure poly(TEEMA) (−60 °C), while the other (60 °C) is intermediate between the T_g for pure poly(TEEMA) and that for pure PVP (180 °C). The PVP component which is trapped in the miscible PVP–TEEMA phase would behave similarly to that in a homogeneous PVP–TEEMA membrane, i.e. PVP extractability is strongly reduced. In fact, the PVP diffusivity similar to that in other blends reported in Table 2 indicates that a fraction of PVP, the easily extractable one, was in a physicochemical environment similar to that in other blend materials, whereas the other fraction was hardly extractable.

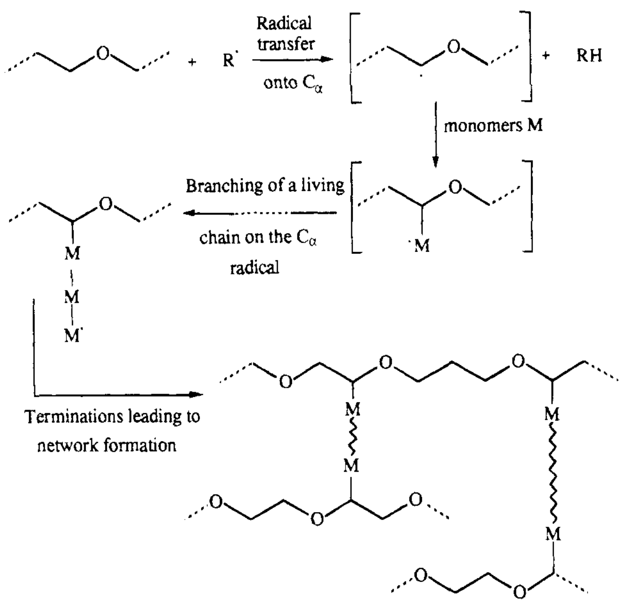


Figure 7. Schematic representation of network formation by radical transfer onto ether $C\alpha$, branching of monomers and finally termination reactions.

In order to elucidate the mechanism of partial PVP retention by the poly(TEEMA) component in the interpenetrating blend, we tried first to see if PVP chains can be covalently attached to the nonsoluble polymer. Simple extraction experiments carried out on several PVP–methacrylate and –acrylate IPBs led us to discard the hypothesis of covalent bonding of PVP chains to methacrylate (or acrylate)-type polymers. As total extraction was observed with alkyl methacrylates, we conclude that there is very low probability of covalent bond formation by recombination of the radicals eventually created on PVP chains by a transfer reaction from living poly(methacrylate) chains. Furthermore, as the 2-(2-ethoxy-2-ethoxyethoxy)ethyl lateral group has no special reactivity to PVP, no covalent bond is expected between the lateral group and PVP.

Another possible mechanism is the formation of a cross-linked network of the nonsoluble polymer: segments of a chemically cross-linked network would impede much more effectively PVP chain reptation than a simply entangled polymer material for which disentanglement occurs in time. For the TEEMA monomer which contains series of three ethoxy units on its pendent chain, an abstraction of the hydrogen atom born by a carbon atom in α-position with respect to the ether function (noted H_α) is possible (Figure 7). Combination of such a radical with another one will generate rings (intrachain combination) or cross-links (interchain combination). In order to know whether such reaction was possible under our photopolymerization conditions, we irradiated methacrylate (and acrylate) monomers in the presence of a photoinitiator but without the PVP component. The obtained materials were then submitted to dissolution tests in good solvents of the polymer (e.g. acetone, DMF, DMSO). The results are summarized in Table 3. The 2-methoxyethyl acrylate, similar to TEEMA monomer, gave rise to insoluble materials in the presence of methylether benzoin. But the *n*-butyl acrylate monomer, which differs from 2-methoxyethyl component only by a methylene group instead of the oxygen atom, gave rise to soluble polymer. The presence of a labile hydrogen H_α atom was then needed for a cross-linked network formation. A further experiment showed the effective lability of the H_α:benzophenone, a photoinitiator which works on the basis of hydrogen abstraction mechanism,[26,27] was able to initiate a photopolymerization of TEEMA (and 2-methoxyethyl acrylate) but not that of *n*-butyl acrylate (which contains no ether groups).

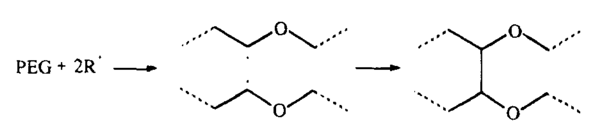


Figure 8. Schematic representation of network formation by two radical transfers onto PEG chains and coupling.

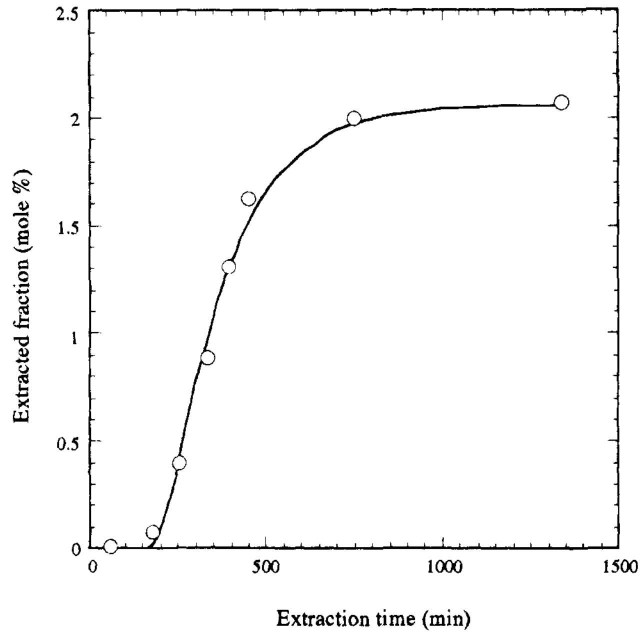


Figure 9. PVP extraction kinetics of PVP_{160000}–EGDMA 75–25 s-IPNs: experimental points and best-fit curve (eq 2 with *D* values from Table 4).

The presence of alkyl ether groups is a prerequisite condition, but their presence may not be sufficient to lead to a cross-linked network. For instance, a 24-h irradiation of a poly(ethylene glycol) of molecular weight 600 led to 10% increase in vicosity but not to an effective cross-linking. This is probably due to the fact that only a bond generated by the combination of two radicals is possible in this case (Figure 8). Such a radical combination would be less probable than chain initiation or termination (Figure 7). In summary, the effective cross-linking of TEEMA could be explained by a polymerization reaction of the monoacrylate accompanied by a certain proportion of transfer reaction on the carbon atom in α-position with respect to the lateral chain ether function. The cross-linking of the poly(TEEMA) promoted a blocking action on some PVP chains.

PVP-Containing Semiinterpenetrating Network (s-IPN). The effect of network structure on PVP extraction was next studied by using PVP-containing semiinterpenetrating networks. The networks were formed from dimethacrylate monomers by photopolymerization in the presence of PVP. Mathematic fitting by eq 2 is in very good agreement with experimental data as shown by Figure 9.

When dimethacrylates of different chain lengths between the two polymerizable double bonds were used to form the s-IPN networks, the extracted fraction of PVP increased as spacer length increased (Figure 10). Both the extractability and diffusivity appear to depend on the mesh size of the network; as expected, the larger the mesh size, the better the PVP extractability and

Table 3. Experimental Results of Some Photoirradiation Experiments and Comments Concerning the Solubility or the Viscosity of the Obtained Materials

irradiated product	photoinitiator	observations
TEEMA	methyl ether benzoin	insoluble polymer
2-methoxyethyl acrylate	methyl ether benzoin	insoluble polymer
n-Butyl acrylate	methyl ether benzoin	soluble polymer
TEEMA	benzophenone	insoluble polymer
2-methoxyethyl acrylate	benzophenone	insoluble polymer
n-butyl acrylate	benzophenone	no polymer formation
PEG600	methyl ether benzoin	slight viscosity increase with UV exposure time

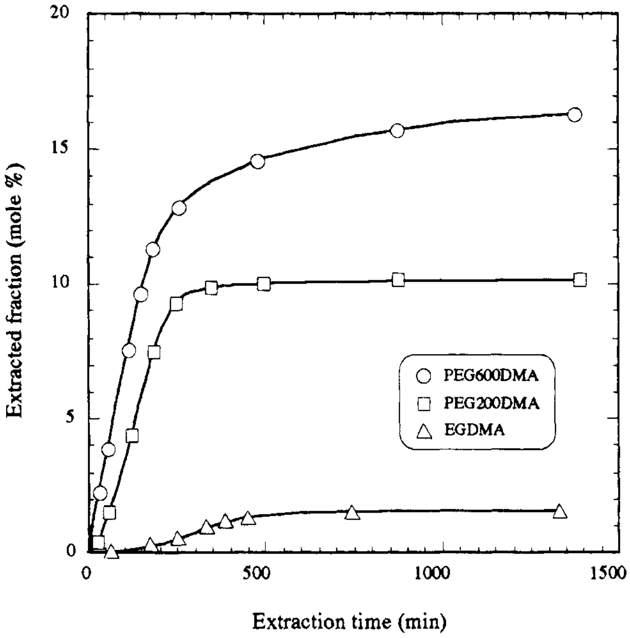


Figure 10. PVP extraction kinetics of PVP$_{360000}$–dimethacrylate 75–25 s-IPNs of different natures.

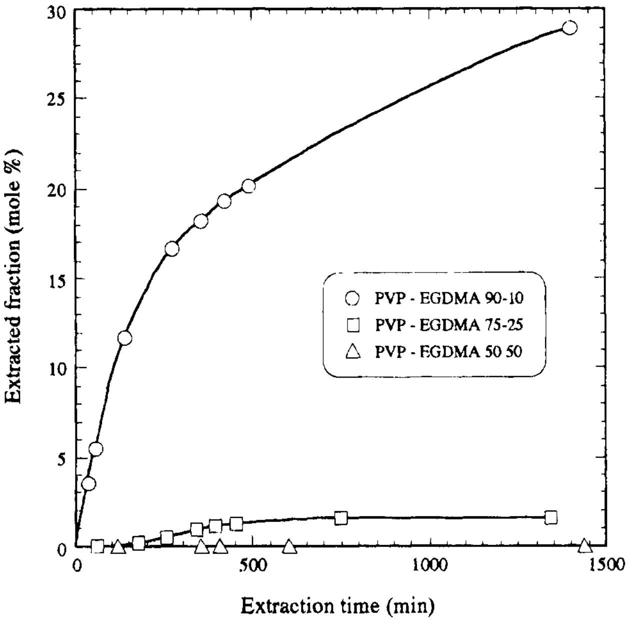


Figure 11. PVP extraction kinetics of PVP$_{360000}$–EGDMA s-IPNs with different PVP/EGDMA ratios.

Table 4. Twenty-Four Hour Extraction of Some PVP-Methacrylate s-IPNs by Stirred Distilled Water at 60 °C[a]

formulation used	PVP extraction rate (mole unit %)	$D_{\mathrm{PVP}} \times 10^9$ (cm^2/s)
PVP$_{40000}$–EGDMA 75–25	4.7	0.02
PVP$_{160000}$–EGDMA 75–25	2.1	0.006
PVP$_{360000}$–EGDMA 75–25	1.6	0.004
PVP$_{360000}$–PEG200DMA 75–25	10.1	0.9
PVP$_{360000}$–PEG600DMA 75–25	16.3	3
PVP$_{360000}$–EGDMA 90–10	28.9	1
PVP$_{360000}$–EGDMA 50–50	0	

[a] PVP diffusion coefficients D_{PVP} obtained by fitting with eq 2 fitting.

diffusivity (Table 4). However, at a fixed PVP/dimethyacrylate ratio, a change in the spacer length also affects the density of entanglement with segments of limited motions (cross-linked segments). By changing the PVP/dimethacrylate ratio of the PVP–EGDMA system, we expect to modify the entanglement density of PVP chains with the cross-linked polymer without affecting the mesh size of the network. The extraction data (Figure 11) shows that an increase in the entanglement density (with dimethacrylate chains) drastically reduces the PVP extractability. For a material containing 10 mol % of the network forming monomer, the 24-h extracted fraction was 28.9% and was still increasing, whereas that containing 25% of the network-forming polymer was stabilized at 1.6% (Table 4); PVP was then no longer extractable from a s-IPN containing 50% the EGDMA monomer.

The diffusivity of extractable PVP chains also sharply decreases with increasing fraction of the network forming monomer: an increase of the value of the latter parameter from 10 to 25% leads to a 3-order of magnitude decrease in PVP diffusivity (Table 4).

The influence of the molecular weight of the soluble PVP polymer was studied using polydisperse fractions of different molecular weights. The extraction kinetics data (Figure 12 and Table 4) show a strong influence of PVP molecular weight on both the extractability and diffusivity of interpenetrated PVP chains.

Again, the dependence of the extractability on the molecular weight of the soluble polymer is hardly explainable by the reptation mechanism. This most striking feature will be discussed in the next paragraph. Concerning the diffusivity of PVP chains in the cross-linked matrix, we found that the dependence of D on the molecular weight M is much weaker than that predicted by the reptation theory for two chemically identical polymers:[22] the diffusion coefficient should scale like M^{-2}, instead of scaling like $M^{-0.75}$. However, the determined scaling exponent is only an indication of the molecular weight dependence, as the used PVP fractions were polydisperse ones.

General Discussion. Our results indicate that the degree of entanglement between the extractable polymer and the nonsoluble cross-linked chain plays a very important role in the extraction of a linear chain by a solvent. The high degree of interpenetration between the linear polymer and the cross-linked matrix would induce an efficient topological trapping of the linear polymer during the cross-linking of poly(dimethacrylate). Although several theoretical works exist in the

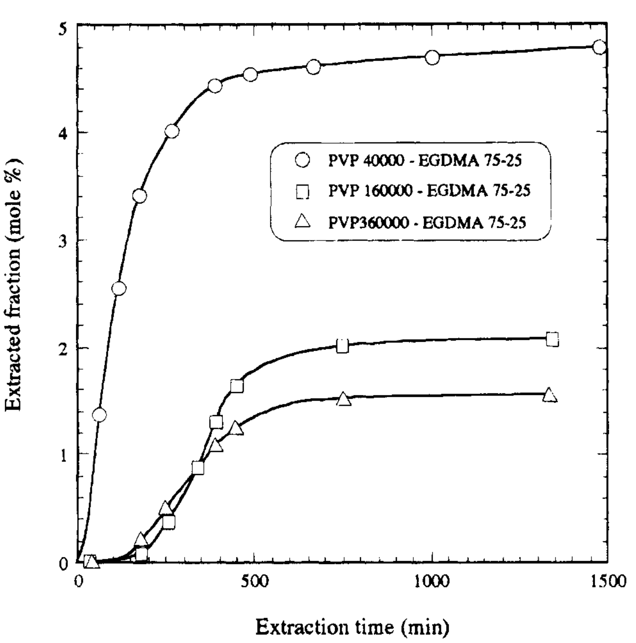


Figure 12. PVP extraction kinetics of PVP–EGDMA s-IPNs with PVP of different molecular weights at a PVP/EGDMA ratio of 75/25.

field of kinetics of polymer–polymer interdiffusion, validations of the theories were most generally performed on polymers of chemically identical nature.[15,16,28,29] The very few experimental studies[30,31] of polymers of different natures, concerned the interdiffusion of two pure polymers which were put into contact. Furthermore, our systems and experimental procedures were far from those assumed to be valid in the theoretical descriptions (e.g. polydispersed polymers, possibility of nonuniformly cross-linked matrix). Another delicate point is the possible change in the blend or s-IPN with time due to extraction of PVP. As the extraction fraction may be large, the thickness reduction may also be large if the nonsoluble polymer can collapse upon departure of PVP chains. If the nonsoluble polymer cannot collapse, then we will deal with a migration of PVP in a porous material whose porosity increases with time due to PVP departure from the solid material. The collapsibility of the nonsoluble polymer component depends on whether the temperature of the studied systems is far above or far below the glass transition temperature (T_g) of the nonsoluble component in the presence of water: in the rubbery state the polymer will collapse whereas it will not when it is in the glassy state. Among the nonsoluble polymers used, only P(MMA) is a glassy polymer (T_g = 121 °C). However, as the T_g decreases upon solvent sorption, P(MMA) may be in the rubbery state in our experimental conditions.

The predicted effects of the situations in which the nonsoluble polymer collapses or does not collapse upon extraction of the soluble component are the following:

(1) If the nonsoluble polymer collapses, the thickness of the slab decreases with the extracted fraction, and the PVP extraction rate into the external medium increases faster than that given by its own diffusivity. This amounts to saying that the "observed" diffusivity increases with time (i.e. with the PVP extraction).

(2) If it does not collapse, the extraction rate depends on the geometrical factors of the porous medium created by the extraction of PVP chains. As the material porosity increases with the PVP extracted fraction, the PVP diffusivity increases with time as well.

Our kinetics data did not show a clear increase in the diffusivity with time. The number of extracted fractions measured in the early stage in the cases of blends was small due to experimental difficulties (short times) and does not allows us to evidence an effective increase in diffusivity. In the cases of s-IPN, no significant increase in diffusivity was detected (estimated by the departure of the experimental points from the calculated curves obtained with constant diffusivity) (Figures 10–12). The slow drift of the extracted fraction with time in the late stage should be attributed to a slow additional PVP extraction rather than any increase in the diffusivity. It appears to us that the change in the volume or the structure of the studied materials during extraction did not have a large influence on the results.

The most salient feature emerging from our results is the nonextractability (or very low extractability) of a fraction of PVP chains, when they are interpenetrated by a chemically cross-linked network. This fraction of polymer chains, whose dynamic properties are different from the fraction having the classical dynamic properties of unattached chains, increases rapidly with the dimethacrylate content, i.e. with the cross-linking density. Such a behavior contrasts with that observed by Mark and Zhang[9] who reported a complete extraction of poly(dimethylsiloxane) linear chains through a cross-linked PDMS network. The different natures of the linear polymer could not induce the observed blocking (or strong hindering) of the linear chain. Indeed, PVP chains interpenetrated by P(HEMA), a polymer which is bound to PVP by strong hydrogen bonds, were quasitotally extracted by water (Figure 4). The water molecules must release the PVP chains from the hydrogen bonds with P(HEMA) thanks to the ability of hydrogen bonding of the solvent. Furthermore, the chemical potential driving force existing in the system is high enough for the extraction and the leveling off could not be due to a lack of driving force. Indeed, when we put in pure water an s-IPN sample which had no longer released PVP in the extracting medium, we did not observe any further PVP release from the sample.

In order to explain how an entangled chain cannot move through the cross-linked network, we would like to emphasize that the average chain lengths between cross-links for the systems used in the present work were much shorter than the ones used by Mark and Zhang (who used a network with chains of molecular weight 12 000 between cross-links). According to the reptation model, the chains move curvilinearly along the tube formed by other chains. The diameter of the tube is the distance between entanglements, which is about 50 Å.[22] But a chain interpenetrated by other chains *in situ* formed by polymerization of monomers may be intricately entangled at very short distances. There would be multiple PVP loops or eventually nooses around different branches of the dimethacrylate network as a consequence of a chain growth by addition of monomer molecules which solvate the PVP chains. Due to the high density of cross-links, a chain may be knotted many times on a short spatial distance (Figure 13). The topological constraints here would then be very different from those of two entangled linear chains of the same chemical nature. A chain many-fold knotted in a short distance would have much more difficulty to undo the knots when it is subjected to a pulling force (chemical potential). As the pulling forces are exerted on several parts of the chain (due to contact with the solvent medium which diffuses rapidly toward the

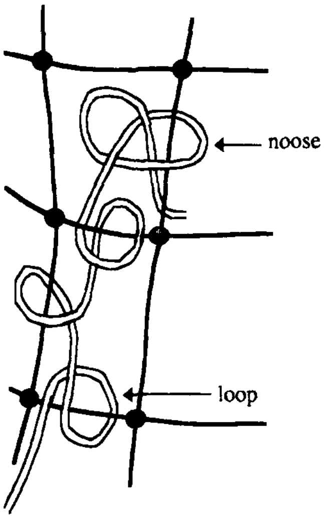


Figure 13. Schematic representation of entanglements at very short distance in s-IPNs.

chain), such a chain would have a great difficulty to move due to a snaring effect. As the knotting depends on the (random) walk of the growing chain, it is understandable that at higher contents of dimethacrylate, more chains are locked in close knots and become much less extractable.

The obtained results, as a whole, seem to be consistent with the proposed interpretation:

No blocking of the linear PVP chains in blends with P(MMA) and in IPBs with P(HEMA), even at high contents of the latter polymers.

Partial blocking of PVP chains in the case of IPBs with P(TEEMA) in which there would be cross-links of small mesh size.

Partial blocking of PVP chains in all s-IPNs with poly(dimethacrylate). The smaller the mesh size or the higher the cross-linked matrix content, the larger the blocking effect.

Due to the high PVP proportion in the s-IPNs, it is quite understandable that a fraction of PVP chains can be extracted out of the material. The chains of this fraction would be entangled with the nonsoluble polymer network in a different way (lesser entanglement points with the cross-linked matrix) than chains of the nonextractable fraction. The diffusivity of extractable PVP chains decreases, as expected, with the decrease in the mesh size or with the increase in the proportion of the cross-linked network (larger topological constraints on confined chains).

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