

Solubility Characteristics of Poly(4-Methyl-1-Pentene)

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SYNOPSIS

Relative solubility determinations in over 50 compounds have identified numerous good solvents as well as nonsolvents for poly(4-methyl-1-pentene) (TPX) at elevated temperatures. The better solvents include hydrocarbons and esters that contain significant amounts of aliphatic or cycloaliphatic character. Equilibrium phase-transition temperatures for dissolution upon heating and phase separation upon cooling were determined by a hot-stage light microscopic method. The significance of the results is related to the ability to determine precisely the relative solvent power of different solvents and related to the preparation of permselective membranes from the polymer solutions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(4-methyl-1-pentene), also known as TPX, is a clear, high melting, crystalline polymer with potential utility as a permselective membrane and/or membrane support for separation of gas mixtures. Asymmetric hollow TPX fibers, for example, containing a very thin discriminating outer "skin" supported by a porous matrix might result in the use of thin-wall membranes that could result in faster gas transport with minimal changes in selectivity when compared to similar homogeneous membranes.¹ Such membranes may be made by the proper extrusion ("spinning") of polymers, solvent, nonsolvent, or plasticizer mixtures followed by removal of the one or more liquids to leave the neat polymer fiber. Such techniques require knowledge of the solubility characteristics of the polymer and ultimately a description of the pertinent phase equilibria. The preparation of composite membranes in which a porous matrix polymer supports a thin discriminating layer of a different polymer also requires a knowledge of the polymers' solubility characteristics.²

Ideally and from a practical standpoint a "good" solvent for polymers for membrane formation might be envisioned to have numerous desirable charac-

teristics. These would include: (a) good solvent power over a wide concentration range; (b) a relatively high boiling point; (c) a high flash point; (d) low toxicity; (e) noncorrosive and noncaustic properties; (f) good thermal stability at elevated temperatures; (g) a relatively high solubility-temperature coefficient; (h) solid formation below about room temperature; (i) a very low vapor pressure at ambient temperature; (j) considerable solubility in various other liquids that are nonsolvents for the polymer; (k) a low density; (l) inexpensiveness; (m) ready availability; and (n) preferably, significant solubility in water. It is probable that no compound possesses all of these characteristics, but its potential usefulness may be ascertained by judicious comparison with these standards.

The solubility parameter of TPX is calculated to be about 7.4–8.0 (cal/cm³)^{1/2}.^{3,4} This suggests that certain alkanes, cycloalkanes, or aliphatic esters or ketones might be effective solvents.⁵ (The solubility parameter does not address the energy barrier to solution presented by the polymer crystallinity and thus, from a practical standpoint, may tend to be misleading.) Numerous solvents have been reported for TPX (Chemical Abstracts registry number 24979-98-4). "Solvents" reported include halogenated hydrocarbons such as *o*-dichlorobenzene, *m*-chlorotoluene, carbon tetrachloride, chlorobenzene, fluorobenzene, 1,2,3-trichloropropane, trichloroethylene, chloroform, fluorobenzene, methylene chloride, and perchloroethylene⁶⁻⁹; aromatic hydrocarbons such as xylene, Tetralin, toluene, and

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Table I Solvents for Poly(4-Methyl-1-Pentene)

Compound	Approximate Boiling Point (°C)	Approximate Solubility (wt %)	Temperature (°C)
Acetone	56	—	—
Methyl acetate	57.5	< 1.0	62
Chloroform	61	< 0.6 ^a	62
Methanol	65	—	—
Perfluoro(methylcyclohexane)	76	< 2.7	76
Ethanol	78	—	—
Cyclohexane	81	20–26	80
2-Propanol	82	—	—
Trichloroethylene	87	< 1.3 ^a	102
Methylcyclohexane	101	> 26	102
Acetic acid (glacial)	117.5	< 0.9	120
Perchloroethylene	121	> 1.2	150
Perfluorodecalin ^b	142	< 2.5	142
Cyclohexanone	155	< 1.0	102
<i>i</i> -Propylcyclohexane	155	> 32	154
1-Hexanol	156.5	< 2.4	153
Diethylene glycol dimethyl ether	162	< 1.6 ^c	168
<i>t</i> -Butylcyclohexane	167	> 31	154
Cyclohexyl acetate	173	> 41 ^d	172
<i>o</i> -Dichlorobenzene	180	> 30	180
Dimethylsulfoxide	189	< 7.9	186
Decahydronaphthalene ^b	190	> 39	190
Ethylene glycol	197	< 7.8	186
2-Ethylhexyl acetate	199	> 1.1	170
1-Methyl-2-pyrrolidinone	202	< 8.4	186
Acetophenone	202	< 8.4	150
		< 8.4	186 ^c
Tetrahydronaphthalene	207	> 30	190
<i>n</i> -Octyl acetate	211	> 50 ^d	210
1,2,4-Trichlorobenzene	214	> 25	170
Perfluorodecahydrophenanthrene	215	< 3.0 ^c	222
Triethylene glycol dimethyl ether	216	< 1.6 ^c	196
Dodecane	216	> 52 ^d	197
Dicyclohexyl	227	> 36 ^d	212
Cyclohexylbenzene	240	> 41 ^d	212
Biphenyl	255	< 0.9 ^c	170
Diethylene glycol dibutyl ether	256	> 16	196
		> 50 ^d	234
Diphenyl ether	259	< 8.1	150
		< 8.1 ^a	186
Methyl laurate	262	> 52 ^d	210
Decanoic acid	269	> 19 ^a	205
Tetraethylene glycol dimethyl ether	275	< 1.5 ^c	196
		< 8.6 ^c	235
Dimethyl phthalate	282	< 7.4 ^c	186
		< 7.4 ^c	235
Sulfolane	285	< 7.0	235
Hexadecane	287	> 54 ^d	210
Castor oil	313	< 1.6	241
Methyl myristate	323	> 60 ^d	220
HB-40 ^e	~ 325	> 26	205

Table I (Continued)

Compound	Approximate Boiling Point (°C)	Approximate Solubility (wt %)	Temperature (°C)
Butyl stearate	343	50–60 ^d	220
		> 60 ^d	233
Methyl stearate	~ 359	< 41	215
		> 41	225
Mineral oil	~ 360	> 55 ^d	223
		> 75 ^d	248
Dioctyl phthalate	384	< 8.8 ^c	186
		< 8.8 ^c	235
Paraffin oil	—	< 41 ^{a,d}	220
		> 40 ^d	231
Polyethylene glycol, E400 ^f	—	< 0.8	150
		< 7.7	186
Poly(dimethylsiloxane), 50 cps viscosity	—	< 1.1 ^c	212
		< 40	243

^a Badly swollen and partially soluble.

^b *cis-trans* mixture.

^c Some attack and possible partial dissolution.

^d Consistency of candle wax at room temperature.

^e "Hydrogenated terphenyl," Monsanto Industrial Chemicals Company.

^f The Dow Chemical Company.

^g 40 cps viscosity (Brookfield, 140°C).

naphthalene^{6,9-12}; alkanes and cycloalkanes such as Decalin, hexadecane, cyclohexane, hexane, and pentane^{1,9-12}; and olefins such as cyclohexene and hexadecene.^{13,14} Also reported are esters such as amyl acetate, butyl benzoate, and dihexyl sebacate^{12,13}; alcohols such as dodecanol and undecanol¹³; amines such as dodecylamine¹³; ethers such diphenyl ether and dibenzyl ether^{10,13}; acids such as decanoic acid¹³; and miscellaneous compounds such as carbon disulfide.^{12,15} Many of these compounds can be rejected as practical solvents for the preparation of TPX membranes by applying the aforementioned criteria for a good solvent. In general the literature references cited tend to be nonspecific concerning the details of polymer solubility. Elevated temperatures were often specified for dissolution, and the resulting solution concentrations, when reported, were low, for example, less than about 10%. An available industrial product bulletin¹⁶ lists the relative chemical resistance of injection-molded TPX specimens when exposed over a period of 3 months to 202 different organic and inorganic liquids at 20°C and 60°C. These data indicate that a number of aliphatic, cycloaliphatic, and aromatic hydrocarbons, esters, and chlorinated hydrocarbons may be effective solvents for TPX under the proper conditions.

This paper presents selected and exploratory solubility studies for TPX and the equilibrium binary-phase diagrams for the polymer and several "preferred" solvents and solvent mixtures.

EXPERIMENTAL

The TPX polymers used were designated as RT-18 and DX-810 (Mitsui Petrochemical Industries, Ltd.). When heated at 10°C/min in a Perkin-Elmer differential scanning calorimeter, Model 1B, RT-18 melted at 235.1°C and DX-810 melted at 231.3°C with a "shoulder" at 233.7°C. After being exposed to a maximum temperature of 267°C, RT-18 froze at 203.8°C with a shoulder at 206.4–208.7°C. DX-810 froze exhibiting two peaks at 206.8°C and 209.7°C. The solvents were obtained from Aldrich Chemical Company and MCB Reagents; they were used without further purification.

Dissolution studies were conducted by visual observations on screw-cap sealed glass vials in an air-circulating oven. Heating with intermediate agitation and mixing was carried out for at least 24 h at temperature and at a temperature precision of ±0.5°C. The concentration of polymer in the soluble

mixtures was increased by subsequent addition of pellets until no further dissolution was observed or until the solution viscosity was so high that flow under gravity was extremely slow. Refractive index differences between "solvent" and TPX generally were sufficiently great to enable one to easily follow the progress of dissolution; the use of Decalin, PEG-400, 1-methyl-2-pyrrolidinone, and mineral oil required more careful observation.

Phase-transition temperatures were observed microscopically with a Leitz Ortholux instrument equipped with phase contrast optics and a Heine condenser. Visual observation was made at 400 \times magnification using an objective lens of 0.40 numerical aperture. Temperature was varied by a calibrated Mettler FP82 hot stage controlled by a Mettler FP80 Central Processor. Slides were prepared by firmly pressing a #1 cover glass on the specimen at maximum temperature. Each slide was cooled at a given rate until the first appearance of a second phase was noted; the temperature was recorded to the nearest 0.1 $^{\circ}$ C. After precipitation appeared to be complete, the sample was then heated at the same rate until dissolution was complete; this temperature was also recorded. The maximum temperature to which each mixture was subjected varied from 190 to 235 $^{\circ}$ C depending upon the boiling point of the solvent and its concentration. Samples of each composition were observed by repeated temperature cycling at cooling and heating rates of 2.5, 5.0, 10.0, 15.0, and 20.0 $^{\circ}$ C/min.

RESULTS AND DISCUSSION

Table I lists 54 compounds or solvents in order of increasing boiling point that were examined for their ability to dissolve TPX (RT-18). The solubilities shown do *not* represent equilibrium values; in all cases the equilibrium solubility is most likely larger than the indicated value. The relative solubilities shown are approximate values only at the indicated temperatures. (No relative values are shown for acetone and for three lower alcohols; these compounds are very effective nonsolvents for the polymer.) All of the mixtures examined showed behavior consistent with an upper critical solution temperature. Several compounds, methyl acetate, trichloroethylene, and perchloroethylene, were examined somewhat above their boiling points under autogenous pressure in the sealed vials. No compounds were found that dissolved any significant amount of polymer at room temperature. A temperature in excess of about 100 $^{\circ}$ C was generally required for significant dissolution to occur.

Typical "better" solvents include: cyclohexane derivatives (e.g., isopropylcyclohexane, *t*-butylcyclohexane, dicyclohexyl, and cyclohexylbenzene); high boiling aliphatic esters (e.g., butyl stearate, *n*-octyl acetate, cyclohexyl acetate, and methyl laurate); and higher-boiling aliphatic hydrocarbons (e.g., Decalin, dodecane, and hexadecane). Cyclohexane has been previously reported as a solvent for TPX (see INTRODUCTION), but its boiling and flash points are too low for most safe and practical membrane applications. By increasing the solvent molecular weight while still retaining a cyclohexane "nucleus" or "character," the accompanying increase in boiling point allows greater polymer dissolution to be obtained. For example, the boiling points of isopropylcyclohexane, cyclohexyl acetate, dicyclohexyl, cyclohexylbenzene, and HB-40 (a hydrogenated terphenyl) are considerably greater than that of cyclohexane. The good solvent power of *n*-octyl acetate and methyl stearate shows that the major hydrocarbon moiety may be present in either the alcohol or acid derived part of the ester. Mineral and paraffin oils are very good solvents for TPX especially at temperatures greater than about 200 $^{\circ}$ C. Many of the more concentrated solutions of TPX in the better solvents become dry homogeneous solids with the consistency of candle wax when cooled to room temperature. Such behavior may be desirable for membrane preparation and properties.¹⁷ Low molecular weight polyethylene wax will not completely dissolve 40 wt % TPX at 243 $^{\circ}$ C; the mixture becomes a heterogeneous mushy/waxy semisolid at room temperature. Optimum solvent effectiveness requires a balance between hydrocarbon molecular weight (and therefore boiling point) and the TPX molecular weight. Thus for membrane applications the use of as high a molecular weight solvent as is reasonably possible without restricting its solvent ability is recommended.

Polymer solubility is normally a function of polymer and solvent molecular weights, the relative solubility parameters, the volume fractions, and the interaction parameters.¹⁸ In this work no obvious correlations were observed between the relative solvent ability of the liquid and its total solubility parameter and that of the polymer. The estimated solubility parameter of TPX is about 7.4–8.0 (cal/cm³)^{1/2}.^{3,4} The better solvents found here range in solubility parameter from about 7.5 to 10.0 with poor and medium hydrogen bonding ability.⁵ However, the poorer solvents ranged in solubility parameter from about 6.1 to 14.6. This observed poor correlation may be a reflection of the elevated temperatures required for dissolution and/or the energy barrier presented by the polymer crystallinity.

Equilibrium phase-transition temperatures as a function of composition were determined for mixtures of TPX (RT-18) and eight of the better solvents by observing the phase separation and dissolution processes by hot-stage phase-contrast light microscopy. A typical microscopic view above and below a phase-transition point is shown in Figure 1. Transition temperatures were observed by repeated heating and cooling of each mixture at rates of 2.5–20°C/min; linear extrapolation of these data to zero rate yielded the equilibrium transition temperatures that are presented in Table II. Finite heating and cooling rates will yield lower “apparent” transition temperatures. Depending upon the solvent, the composition, and the transition direction the coefficients of change of transition temperature with rate vary from about –0.2 to –0.8 min; smaller (i.e., more negative) coefficients were observed upon cooling. A linear plot of the pertinent equilibrium transition temperatures versus concentration is shown in Figure 2 for mixtures of TPX and butyl stearate. Similar curves may be generated for mixtures of TPX and mineral oil or methyl myristate

from the data in Table II. The lower curve represents transitions obtained upon cooling the mixtures; that is, it describes precipitation transitions from homogeneous one-phase solutions to multiphase mixtures. The upper curve represents transitions observed when the multiphase mixtures become homogeneous one-phase solutions upon being heated. Any temperature–composition point above each line represents a one-phase region; any point below each line, a multiphase region. Supercooling amounting to about 13–29°C is evident in all mixtures; the amount of supercooling decreases with increasing polymer concentration. The coefficients for linear and best-fit equations¹⁹ describing these mixtures are shown in Table III. Correlation coefficients of fit for the linear curves are 0.97–1.00. Extrapolation of the best-fit curves to 100% polymer concentration gives values corresponding closely to those measured for the neat polymer by DSC.

A comparison of the cooling and heating transition temperatures at 50% polymer concentration in Table II gives an indication of the relative solvent ability of each of the eight solvents. The lower the

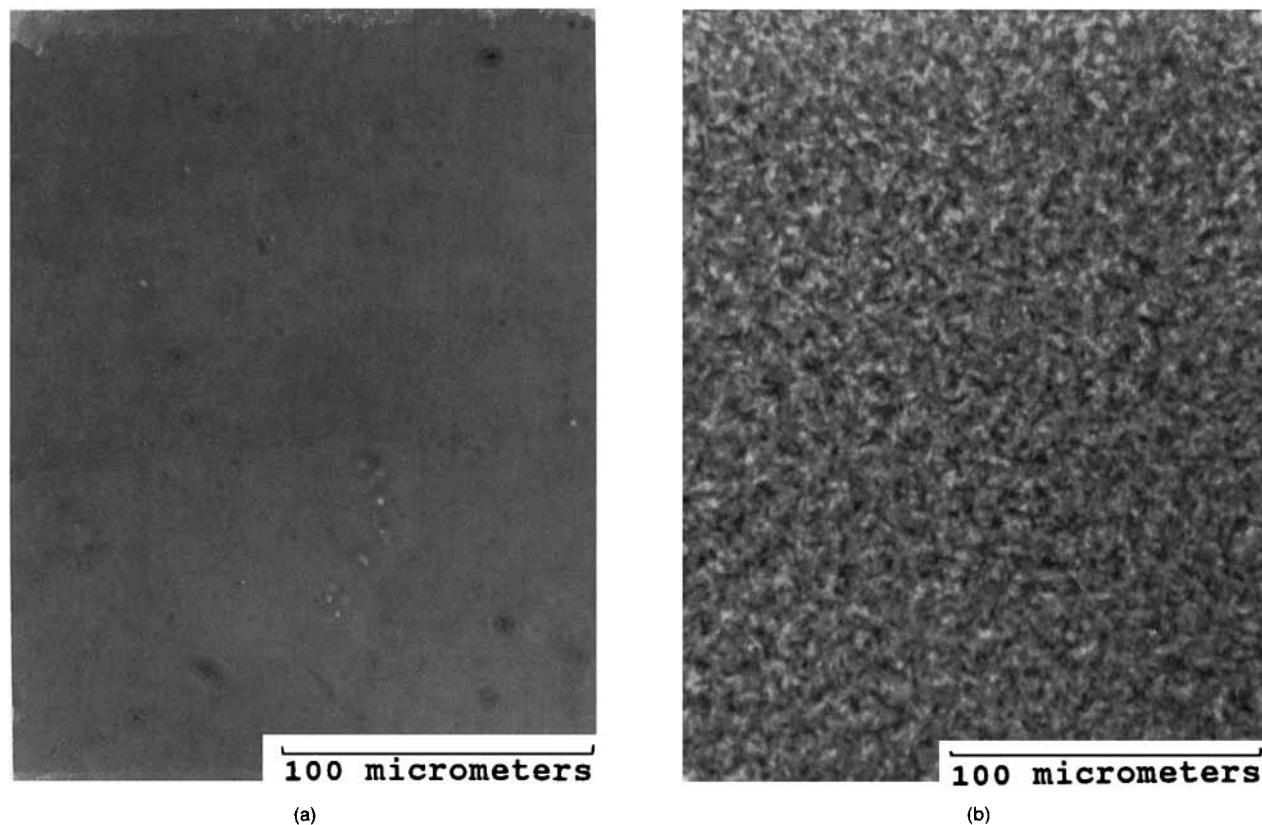


Figure 1 Microscopic views of typical TPX-solvent mixture. 40 wt % TPX in butyl stearate, (a) at 205°C and (b) at 170°C. 400× magnification with phase-contrast illumination.

Table II Mixtures of Poly(4-Methyl-1-Pentene) and Several Solvents

Solvent	Composition (wt % TPX)	Equilibrium Transition Temperature (°C)	
		Cooling	Heating
Butyl stearate	5.08 ^a	175.5	196.7
	10.05 ^a	173.6	197.0
	20.01 ^a	175.5	198.2
	30.02 ^a	179.2	200.3
	40.04 ^a	183.3	204.2
	50.0 ^a	188.8	208.6
	59.97 ^a	192.4	210.6
	69.89 ^a	199.2	216.7
	79.87 ^b	206.8	221.6
	89.78 ^c	215.5	228.9
Mineral oil	10.03 ^a	165.0	189.6
	25.00 ^a	173.4	196.5
	49.97 ^a	185.9	207.2
	74.90 ^b	201.4	218.5
	89.78 ^c	212.3	227.9
Methyl myristate	10.05 ^a	162.2	180.6
	25.01 ^a	164.8	187.3
	50.0 ^a	178.3	199.3
	59.75 ^a	182.3	203.4
	74.96 ^a	194.9	211.7
Dodecane	89.77 ^d	210.8	225.1
	50.0 ^e	149.8	179.1
Diethylene glycol dibutyl ether	50.08 ^a	169.8	193.6
<i>n</i> -Octyl acetate	49.66 ^e	158.8	183.8
Hexadecane	54.08 ^a	172.2	195.4
Methyl laurate	52.13 ^a	174.3	196.9

^a Maximum temperature, 220°C.

^b Maximum temperature, 225°C.

^c Maximum temperature, 235°C.

^d Maximum temperature, 230°C.

^e Maximum temperature, 190°C.

transition temperature, the better the solvent power of the compound; that is, the lower the temperature required to achieve complete dissolution, the better the solvent. The data suggest the following solvent abilities in order of decreasing solvent power: [best] dodecane > *n*-octyl acetate > diethylene glycol dibutyl ether > hexadecane > methyl laurate > methyl myristate > mineral oil > butyl stearate [worst]. The solubility parameters of these solvents range from about 7.1 to 8.6, in modest agreement with the calculated values for the polymer.

The minor compositional differences, if any, between polymers RT-18 and DX-810 are not known for certain, but their DSC behaviors are slightly different (see EXPERIMENTAL). A comparison of

their equilibrium transition temperatures at about 50% polymer concentration in three solvents is shown in Table IV. The slight solubility differences shown are not considered to be significant within the experimental error of measurement.

Equilibrium phase-transition temperatures for mixtures of TPX (RT-18) in solvent mixtures are shown in Table V. The transition temperatures for mixtures in butyl stearate-hexadecane are approximately linear with respect to composition; correlation coefficients of fit are in excess of 0.96. (A slightly better fit is given by $\text{Temperature} = AC^{(BC)}$, where A and B are equation constants, and C is the concentration of the solvent mixture; correlation coefficients are in excess of 0.98.) The supercoolings of about 19–23°C are similar to those observed with the neat solvents; supercooling generally increased with increasing concentration of the lower boiling solvent component, hexadecane. Table V also contains transition temperatures for mixtures of approximately 50% TPX and solvent mixtures composed of about 25% each of methyl myristate and *n*-octyl acetate, methyl laurate and dodecane, and mineral oil and diethylene glycol dibutyl ether. The data are limited in the number of observations made (three), but the temperatures measured are linear with solvent composition (correlation coefficients in excess of 0.97). Supercoolings are in the range of 21–29°C and also increase with increasing concentration of the lower boiling solvent component. From a practical fiber spinning standpoint this observed linear behavior of transition temperature with solvent composition means that if one knows the precipitation and dissolution temperatures of given TPX solvent mixtures, one can then readily calculate with reasonable certainty the corresponding temperatures for TPX solutions in mixtures of any two of these solvents.

Nonsolvents are frequently a component of membrane spinning compositions in addition to the polymer and good solvent.²⁰ The presence of the nonsolvent may result in a "miscibility gap" over a large range of compositions in the ternary system; this may result in greater control of the membrane forming process by affecting the ease of membrane formation and the resulting cell structure, the permeability, and the porosity. Alcohols and hydroxy-terminated polyglycols are nonsolvents for TPX (Table I). Table V contains equilibrium transition temperatures for mixtures containing about 30, 50, and 70% TPX in butyl stearate containing small amounts of polyethylene glycol E600 or polypropylene glycol P1200. The data confirm the glycols' nonsolvent behavior, that is, their presence raise both the equilibrium dissolution temperatures and

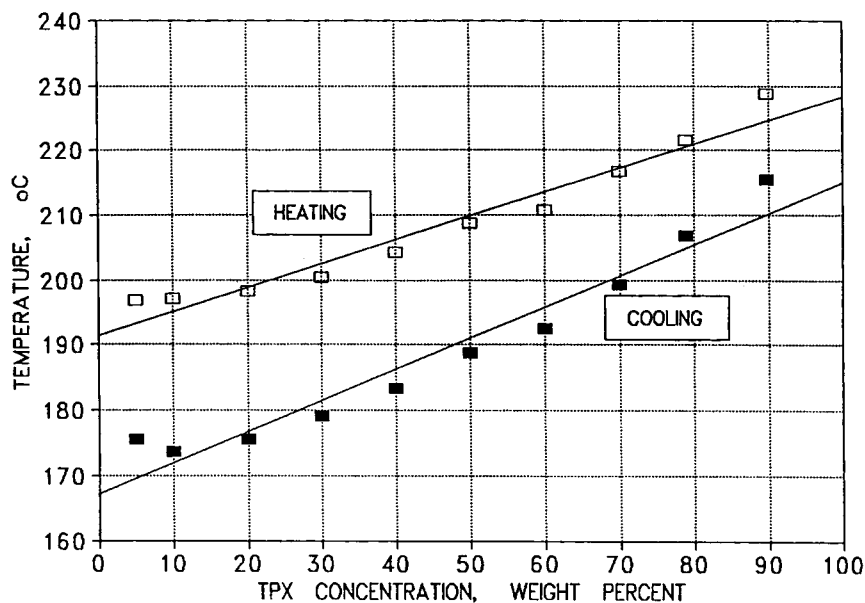


Figure 2 Equilibrium transition temperatures versus polymer concentration for mixtures of poly(4-methyl-1-pentene) and butyl stearate. Linear plots (Table III).

the precipitation temperatures. Polyglycol E600 is a somewhat poorer solvent (or better nonsolvent) than polyglycol P1200 at equivalent concentrations. [Further experiments would be necessary to establish the relative contributions of hydroxyl concentration (E600 has a greater concentration of OH per molecule than P1200), glycol molecular weight, and structure (ethylenic vs. propylenic content) to this observation.] Supercoolings generally were as ex-

pected and in the range of about 17–22°C. At similar concentrations polyglycol E600 reduces supercooling somewhat better than polyglycol P1200. Surprisingly, supercooling was completely eliminated, within the experimental error of measurement, in the sample containing 10% P1200 and 70% TPX. This reduced supercooling was also accompanied by subtle changes in the morphology of the precipitated species that gradually changed with increasing glycol

Table III Best Equations for Three TPX-Solvent Mixtures

Solvent	Mode	Equation	A	B	C	D
Methyl myristate	C	^a	181.9	-608.7	4119.0	4.850E-5
	H	^a	203.9	-551.8	3189.0	3.674E-5
	C	^b	151.4	0.5979	—	—
	H	^b	173.7	0.5334	—	—
Mineral oil	C	^c	164.4	0.3036	2.559E-3	-2658.
	H	^a	214.6	-604.5	3551.0	2.709E-5
	C	^b	158.4	0.5837	—	—
	H	^b	184.5	0.4688	—	—
Butyl stearate	C	^d	169.1	0.3091	125.2	2.547E-5
	H	^e	196.2	0.0519	3.430E-3	—
	C	^b	167.3	0.4757	—	—
	H	^b	191.4	0.3704	—	—

C, cooling; H, heating.

^a $Y = A + B/X + C/X^2 + DX^3$ where Y = temperature, °C; X = concentration of TPX, wt %.

^b $Y = A + BX$.

^c $Y = A + BX + CX^2 + D/X^3$.

^d $Y = A + BX + C/X^2 + DX^3$.

^e $Y = A + BX + CX^2$.

Table IV Comparison of Transition Temperatures of Different Lots of Polymer

Polymer	Solvent	Composition (wt % TPX) ^a	Equilibrium Transition Temperature (°C)	
			Cooling	Heating
RT-18	Butyl stearate	50.0	188.8	208.6
DX-810	Butyl stearate	49.98	188.0	206.6
RT-18	Mineral oil	49.97	185.9	207.2
DX-810	Mineral oil	50.02	185.4	204.9
RT-18	Methyl myristate	50.0	178.3	199.3
DX-810	Methyl myristate	49.98	176.4	198.1

^a Maximum temperature, 220°C.**Table V Mixtures of Poly(4-Methyl-1-Pentene) and Several Solvent Mixtures**

Solvent Mixture (wt %)	Composition (wt % TPX)	Equilibrium Transition Temperature (°C)	
		Cooling	Heating
Butyl stearate	50.0 ^a	188.8	208.6
Butyl stearate (40.01) + hexadecane (10.08)	49.92 ^a	185.8	205.2
Butyl stearate (30.00) + hexadecane (20.00)	50.00 ^a	179.9	201.0
Butyl stearate (19.95) + hexadecane (29.95)	50.10 ^a	177.7	200.1
Butyl stearate (10.08) + hexadecane (40.03)	49.88 ^a	173.8	196.9
Hexadecane	54.08 ^a	172.2	195.4
Methyl myristate	50.0 ^a	178.3	199.3
Methyl myristate (24.98) + <i>n</i> -octyl acetate (25.04)	49.98 ^b	171.6	194.0
<i>n</i> -Octyl acetate	49.66 ^c	158.8	183.8
Methyl laurate	52.13 ^a	174.3	196.9
Methyl laurate (24.98) + dodecane (25.02)	50.00 ^b	163.4	188.4
Dodecane	50.0 ^c	149.8	179.1
Mineral oil	49.97 ^a	185.9	207.2
Mineral oil (24.96) + diethylene glycol dibutyl ether (25.12)	49.92 ^a	177.7	199.7
Diethylene glycol dibutyl ether	50.08 ^a	169.8	193.6
Butyl stearate	30.02 ^a	179.2	200.3
Butyl stearate (65.01) + polyglycol P1200 ^d (5.04)	29.95 ^a	180.8	203.0
Butyl stearate (64.69) + polyglycol E600 ^d (5.25)	30.06 ^a	185.8	204.8
Butyl stearate (59.69) + polyglycol P1200 ^d (10.33)	29.98 ^a	186.2	206.1
Butyl stearate (54.93) + polyglycol P1200 ^d (15.01)	30.06 ^e	188.4	208.2
Butyl stearate	50.0 ^a	188.8	208.6
Butyl stearate (44.79) + polyglycol P1200 ^d (5.33)	49.88 ^a	192.0	211.0
Butyl stearate (44.93) + polyglycol E600 ^d (5.15)	49.92 ^a	194.1	213.3
Butyl stearate (39.90) + polyglycol P1200 ^d (10.18)	49.92 ^e	195.2	213.0
Butyl stearate	69.89 ^a	199.2	216.7
Butyl stearate (24.94) + polyglycol P1200 ^d (5.34)	69.72 ^f	200.9	218.0
Butyl stearate (24.90) + polyglycol E600 ^d (5.05)	70.05 ^e	208.9	221.5
Butyl stearate (20.02) + polyglycol P1200 ^d (10.03)	69.69 ^f	218.5	219.4

^a Maximum temperature, 220°C.^b Maximum temperature, 195°C.^c Maximum temperature, 190°C.^d The Dow Chemical Company.^e Maximum temperature, 225°C.^f Maximum temperature, 230°C.

concentration from the typical "mosaic"-type pattern to a "spherical" or "granular"-type appearance. Thus not only is careful control of supercooling of obvious importance in the physical fabrication of a membrane from a polymer solution, but any such accompanying changes in precipitated polymer morphology might also reasonably be expected to significantly affect the membrane separation properties.

CONCLUSIONS

Numerous good solvents and nonsolvents have been identified for poly(4-methyl-1-pentene). They include hydrocarbons and esters that are rich in aliphatic and/or cycloaliphatic content. Elevated temperatures are generally required for significant dissolution to occur. Phase-transition temperatures may be readily obtained by a light microscopic method that is used to observe samples cooled and heated at various rates; linear extrapolation of these data to zero rate yields the equilibrium transition temperatures. Such information may be used to identify quantitatively the relative solvent ability of different solvents and nonsolvents and their mixtures. Supercooling is generally obtained with these polymer solutions, but it may be modified by the concentration and nature of the solvent or solvent mixture. These techniques and information have importance for the optimum preparation and properties of selected permselective membranes.

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