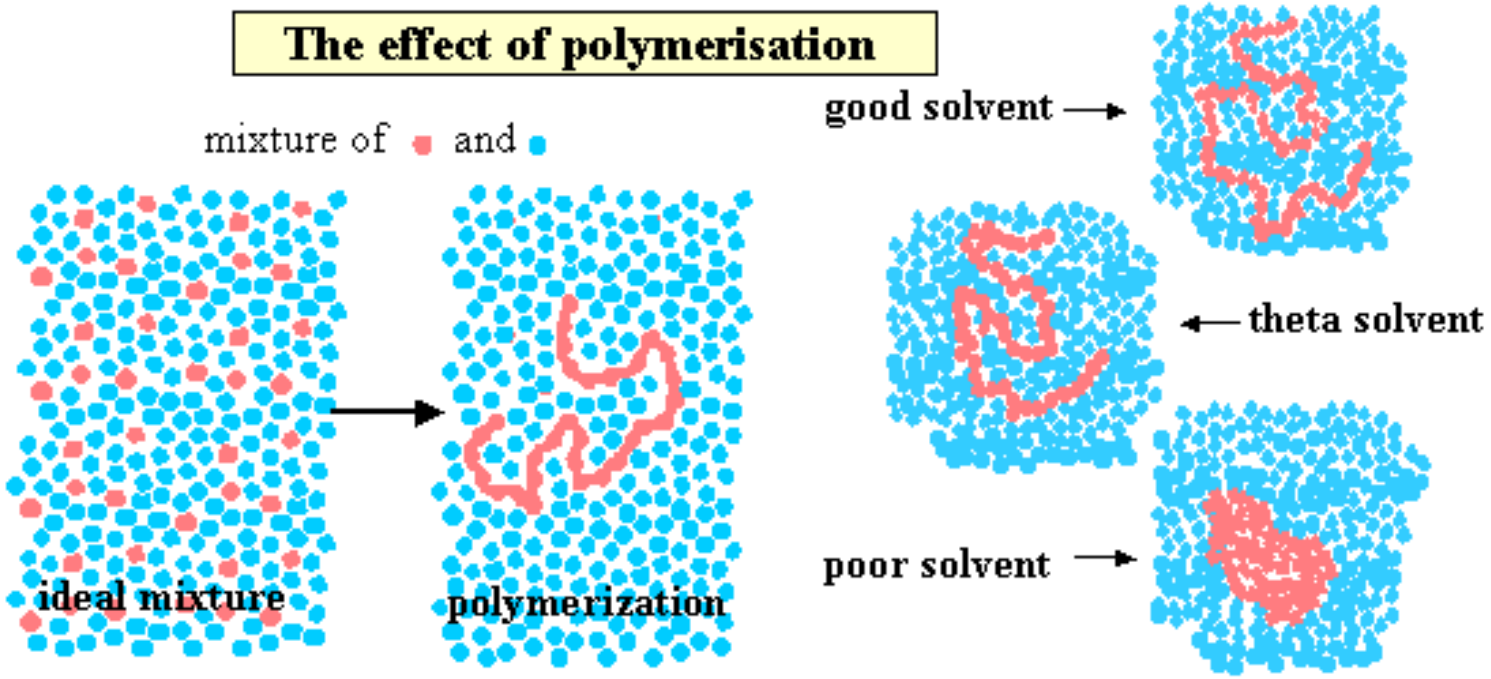
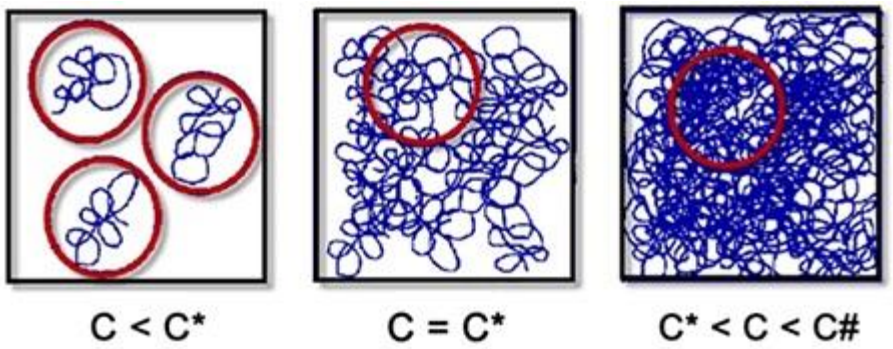
Caracterização de polímeros em solução



http://rkt.chem.ox.ac.uk/lectures/liqsolns/polymer_solutions.html

Questionário inicial:

1) Qual seria o melhor solvente para o polímero?
2) Qual seria a melhor temperatura para dissolver o polímero num dado solvente?
3) Qual seria a faixa de concentração ideal?



Onde achar as respostas?

Solubilidade

$\Delta G_m = \Delta H_m - T\Delta S_m$ Funções de estado

No equilíbrio: $\Delta G_m < 0$

Fatores que afetam a solubilidade

1) Natureza química do polímero e solvente

Parâmetro de solubilidade de Hildebrand (δ), unidade CGS é $(cal/cm^3)^{1/2}$, e SI é $(J.m^3)^{1/2}$.

$$\delta_i = (\Delta E^0_i / V_i)^{1/2}$$

ΔE^0_i = energia de vaporização do solvente puro

V_i = volume molar do solvente

$\delta_2 \rightarrow$ calculado ou determinado pelo grau de intumescimento

$\delta_2 = (\rho \Sigma E / MM_i)^{1/2}$

ρ = densidade

E = constante de atração molecular, MM = massa molar

Solubilidade

$$\Delta H_m = V_m \varphi_1 \varphi_2 (\delta_i - \delta_2)^2$$

Se $(\delta_i - \delta_2) = 0$, solução atérmica $\rightarrow$ **Uso industrial**

Solvente	δ_i $(J.m^3)^{1/2}$	Polímero	$\delta_2 (J.m^3)^{1/2}$
n-hexano	14,8	PE	16,2
Tolueno	18,3	PS	17,6
Acetona	19,9	PMMA	18,6
THF	20,3	PVC	19,4
Metanol	29,7	PET	21,9
Água	47,9	poliacrilonitrila	31,5

Desvantagem: não descreve sistemas envolvendo polímeros semi-cristalinos nem a dependência com MM ou T.

Solubilidade

$\Delta G_m = \Delta H_m - T\Delta S_m$ Funções de estado

No equilíbrio: $\Delta G_m < 0$

Fatores que afetam a solubilidade

Natureza química do polímero e solvente

Parâmetro de solubilidade de Hildebrand (δ), unidade CGS é $(cal/cm^3)^{1/2}$, e SI é $(J.m^3)^{1/2}$. J. H. Hildebran, 1936

$$\delta_i = (\Delta E^0_i / V_i)^{1/2}$$

ΔE^0_i = energia de vaporização do solvente puro

V_i = volume molar do solvente

δ_2 **=>** calculado ou determinado pelo grau de intumescimento

$$\delta_2 = (\rho \Sigma E / MM_i)^{1/2}$$

ρ = densidade

E = constante de atração molar, MM = massa molar

Solubilidade

$$\Delta H_m = V_m \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2$$

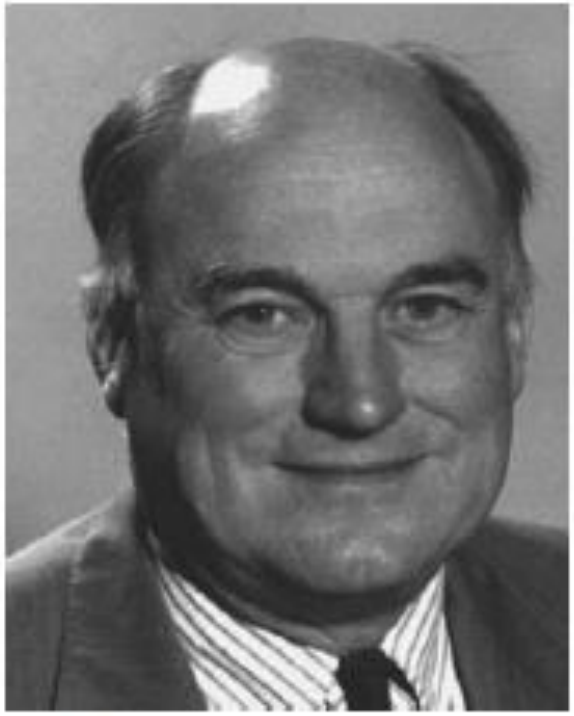
Se $(\delta_1 - \delta_2) = 0$, solução atérmica $\rightarrow$ **Uso industrial**

Solvente	δ_1 (J.m^3)$^{1/2}$	Polímero	δ_2(J.m^3)$^{1/2}$
n-hexano	14,8	PE	16,2
Tolueno	18,3	PS	17,6
Acetona	19,9	PMMA	18,6
THF	20,3	PVC	19,4
Metanol	29,7	PET	21,9
Água	47,9	poliacrilonitrila	31,5

http://cool.conservationus.org/coolaic/sg/bpg/annual/v03/bp03-04.html

Parâmetro de solubilidade de Hansen (δ^2, 1967)

Charles Hansen



Courtesy of Dr C. Hansen. http://hansen-solubility.com/CharlesHansen.html

Charles Hansen is a Danish scientist widely known for the so-called Hansen solubility parameters (HSP). Charles Hansen began his work with solvents in 1962, and almost immediately began producing new and groundbreaking results. Since then, his Hansen solubility parameters have been extensively used and proven valuable to various industries, including coatings, adhesives, plastics, protective clothing and environmental protection. They allow correlations and systematic comparisons previously not possible, such as polymer solubility, swelling and permeation, surface wetting and dewetting, the solubility of organic salts, and many biological applications. Their seemingly universal ability to predict molecular affinities has been generally accepted as being semi-empirical. Charles Hansen published a book summarizing his many years of experience in the field of solubility parameters (Hansen, 2000 and subsequent editions). For a profile of this great scientist and an interesting interview see Meyn (2002).

"Like Dissolves Like"

www.hansen-solubility.com

Parâmetro de solubilidade de Hansen (δ^2, 1967)

$$\delta^2 = \delta_p^2 + \delta_d^2 + \delta_h^2$$

Interações
dipolo permanente /
dipolo permanente

Interações
dipolo induzido /
dipolo induzido

Ligações de H

www.hansen-solubility.com

Appendix 3.1 Hansen solubility parameters (HSP) for selected solvents

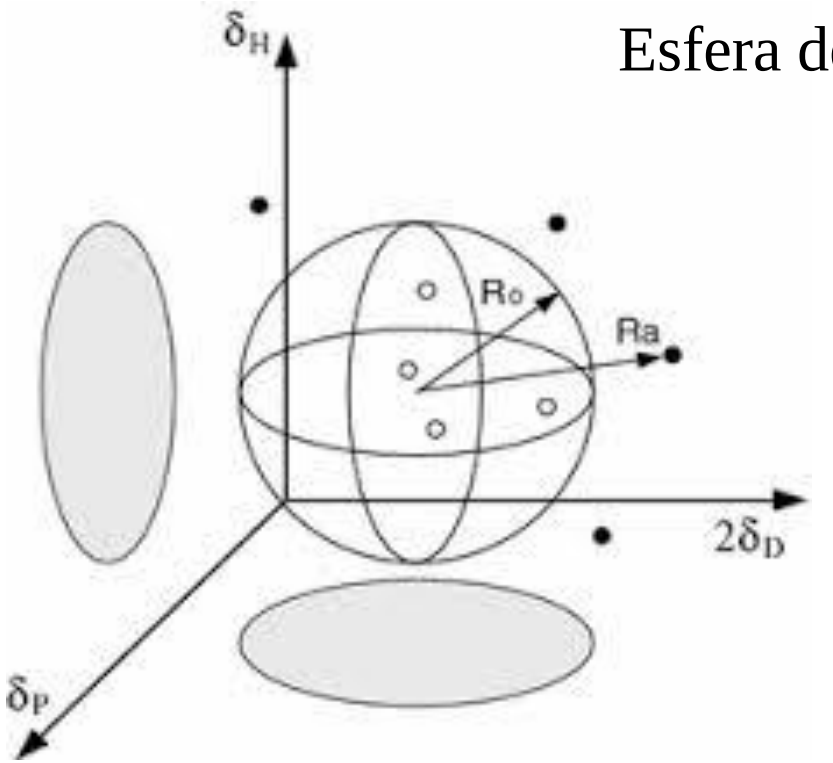
To be used in Equations 3.14 and 3.15. HSP in $(\text{cal cm}^3)^{-1/2}$, V in $\text{cm}^3\ \text{mol}^{-1}$.

Table 3.7 *Solubility parameters of various liquids at 25 °C. For a complete list, see Hansen*

Class	Code	Name	Molar Volume	Parameters		
				δ_d	δ_p	δ_h
Paraffin Hydrocarbons	1	n-Butane	101.4	6.9	0.0	0.0
	2	n-Pentane	116.2	7.1	0.0	0.0
	3	i-Pentane	117.4	6.7	0.0	0.0
	4	n-Hexane	131.6	7.3	0.0	0.0
	5	n-Heptane	147.4	7.5	0.0	0.0
	6	n-Octane	163.5	7.6	0.0	0.0
	7	i-Octane	166.1	7.0	0.0	0.0
	8	n-Nonane	179.7	7.7	0.0	0.0
	9	n-Decane	195.9	7.7	0.0	0.0
	10	n-Dodecane	228.6	7.8	0.0	0.0
	11	n-Hexadecane	294.1	8.0	0.0	0.0
	12	n-Eicosane	359.8	8.1	0.0	0.0
	13	Cyclohexane	108.7	8.2	0.0	0.1
	14	Methyl Cyclohexane	128.3	7.8	0.0	0.5
	14.1	cis-Decalin	156.9	9.2	0.0	0.0
	14.2	trans-Decalin	159.9	8.8	0.0	0.0
Aromatic Hydrocarbons	15	Benzene	89.4	9.0	0.0	1.0
	16	Toluene	106.8	8.8	0.7	1.0
	16.1	Naphthalene	111.5	9.4	1.0	2.9
	17	Styrene	115.6	9.1	0.5	2.0
	18	o-Xylene	121.2	8.7	0.5	1.5
	19	Ethyl Benzene	123.1	8.7	0.3	0.7
	19.1	l-Methyl Naphthalene	138.8	10.1	0.4	2.3
	20	Hesitylene	139.8	8.8	0.0	0.3
	21	Tetralin	136.0	9.6	1.0	1.4
	21.1	Biphenyl	154.1	10.5	0.5	1.0
	22	p-Diethyl Benzene	156.9	8.8	0.0	0.3
Halocarbons	23	Methyl Chloride	55.4	7.5	3.0	1.9
	24	Methylene Dichloride	63.9	8.9	3.1	3.0
	24.1	Chloro Bromo Methane	65.0	8.5	2.8	1.7
	25	Chloro Difluoro Methane	72.9	6.0	3.1	2.8
	26	Dichloro Fluoro Methane	75.4	7.7	1.5	2.8
	27	Ethyl Bromide	76.9	8.1	3.9	2.5
	27.1	1,1 Dichloro Ethylene	79.0	8.3	2.3	1.6
	28	Ethylene Dichloride (1,2 Dichloro Ethane)	79.4	9.3	3.3	2.0
	28.1	Methylene Diiodide[a]	80.5	8.7	1.9	2.7
	29	Chloroform	80.7	8.7	1.5	2.8
	29.1	1,1 Dichloro Ethane	84.8	8.1	4.0	0.2

(continued overleaf)

Parâmetro de solubilidade de Hansen (δ^2, 1967)



Esfera de solubilidade de Hansen (HSP)

Good solvents are within the sphere while bad ones are located on the outside.

www.hansen-solubility.com

Teorias de Hildebrand e Hansen consideraram apenas ΔH_m

✓ Polímeros amorfos, sem variação de temperatura, concentração ou massa molar

X Polímeros semi-cristalinos, variação de T, concentração ou massa molar

Teoria de Flory-Huggins para solubilidade de polímeros

Considerou:

- temperatura
- concentração
- contribuição entrópica

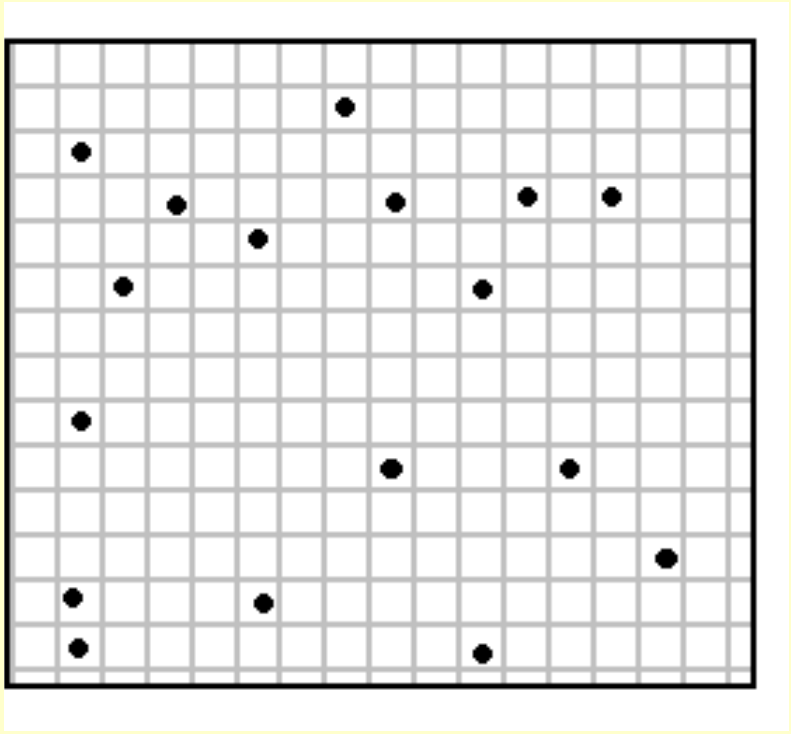
$$\Delta G_m = \Delta H_m - T\Delta S_m$$

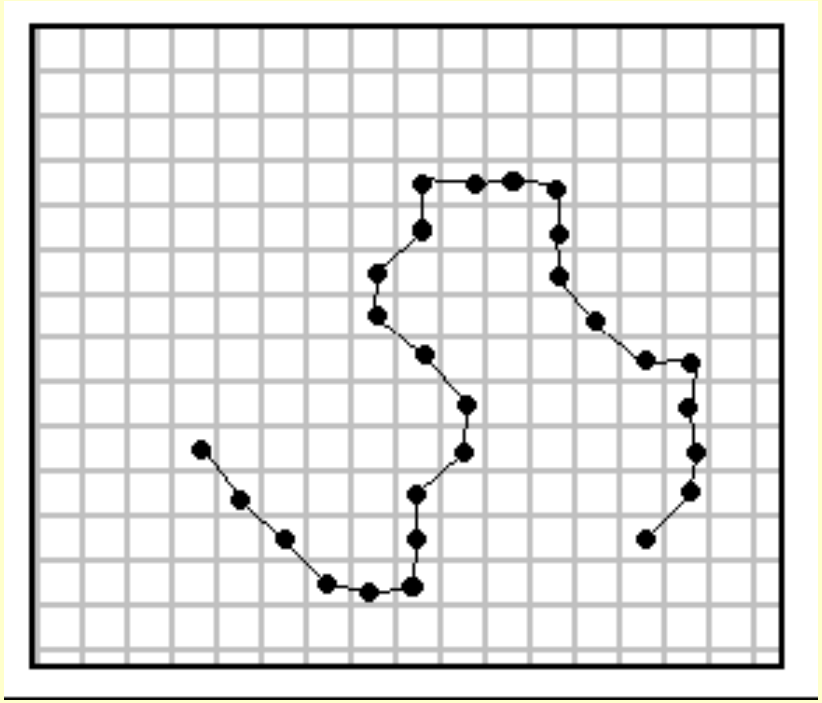
Teoria de Flory-Huggins

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta S_m = k\left[N_1 ln\left(\frac{N_1}{N}\right) + N_2 ln\left(\frac{N_2}{N}\right)\right] \rightarrow \Delta S_m = k\left[N_1 ln\varphi_1 + N_2 ln\varphi_2\right]$$

k = constante de Boltzman, φ_i = fração volumétrica na matriz, N_1 = número de moléculas do solvente e N_2 = numero de moléculas de polímero





An Introduction to Polymer Science, H. G. Elias, 1997.

Teoria de Flory-Huggins

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta S_m = -k\,[N_1 ln\varphi_1 + N_2 ln\varphi_2]$$

$$\Delta H_m = kT\,[N_1 \varphi_2 \chi_{12}]$$

χ_{12} = parâmetro de interação de Flory Huggins, pode depender de T e da concentração

$$\chi_{12} = V_{seg}\,(\delta_1 - \delta_2)^2\,(RT)^{-1} \qquad R = k\,N_A$$

$$\chi(T) = \chi S + \chi H/T$$

$$\Delta G_m = RT\,[n_1 ln\varphi_1 + n_2 ln\varphi_2 + n_1 \varphi_2 \chi_{12}]$$

Contribuição entrópica

Contribuição entálpica

Teoria de Flory-Huggins

Segundo coeficiente de virial $A_2 \rightarrow$ interações soluto/solvente

$$A_2 = \frac{\rho_1}{M_1 \rho_2^2}(0.5 - \chi)$$

$\chi = 0{,}5$ ou $A_2 = 0$ condição theta ($\neq$ interações preferenciais)
$\chi > 0{,}5$ ou $A_2 < 0$ mau solvente (polímero não dissolve)
$\chi < 0{,}5$ ou $A_2 > 0$ bom solvente (polímero dissolve)

Vantagem: descreve a dependência com MM e T

POLYMER-SOLVENT INTERACTION PARAMETERAT INFINITE DILUTION		
Polymer	**Solvent**	χ_∞
Poly(acrylamide)	Water	0.495
Poly(dimethyl siloxane)	2-butanone	0.500
Polyisobutylene	n-Pentane	0.480
Poly(methyl methacrylate)	Acetone	0.480
Poly(p-chlorostyrene)	Toluene	0.475
Polystyrene	Cyclohexane	0.509
Polystyrene	Benzene	0.465
Poly(vinyl alcohol)	Water	0.494

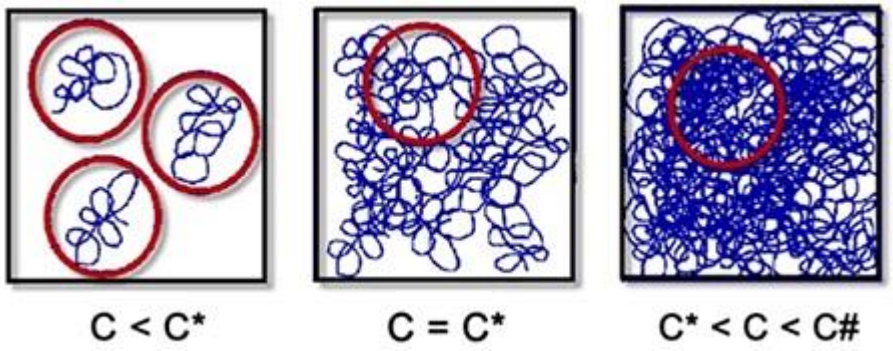
$\chi_{12} = 0{,}5 \rightarrow$ condição theta, não há interações preferenciais

$\chi_{12} < 0{,}5 \rightarrow$ bom solvente

Solvent	EVA 1 (460)			EVA 2 (410)		
	χ	χ_H	χ_S	χ	χ_H	χ_S
$T = 30$ °C						
Cyclohexane	0.490	0.124	0.366	0.563	0.112	0.452
Toluene	0.444	0.043	0.401	0.562	0.045	0.516
Tetrahydrofuran	0.411	0.338	0.073	0.546	0.353	0.193
p-Xylene	0.276	0.015	0.261	0.556	0.016	0.540
Cyclopentane	0.333	0.062	0.271	0.524	0.052	0.472
$T = 40$ °C						
Cyclohexane	0.473	0.125	0.348	0.496	0.113	0.383
Toluene	0.454	0.044	0.411	0.496	0.046	0.444
Tetrahydrofuran	0.417	0.343	0.074	0.487	0.358	0.129
p-Xylene	0.305	0.015	0.290	0.508	0.017	0.492
Cyclopentane	0.337	0.063	0.274	0.455	0.053	0.402
$T = 50$ °C						
Cyclohexane	0.482	0.482	0.127	0.495	0.114	0.380
Toluene	0.461	0.461	0.044	0.495	0.046	0.415
Tetrahydrofuran	0.413	0.413	0.347	0.482	0.362	0.120
p-Xylene	0.347	0.347	0.015	0.471	0.017	0.454
Cyclopentane	–			–		

Questionário inicial:

1) Qual seria o melhor solvente para o polímero?
2) Qual seria a melhor temperatura para dissolver o polímero num dado solvente?
3) Qual seria a faixa de concentração ideal?



POLYMER HANDBOOK

FOURTH EDITION

Editors

J. BRANDRUP, E. H. IMMERGUT, and E. A. GRULKE

Associate Editors

A. ABE
D. R. BLOCH

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS, INC.

New York • Chichester • Weinheim • Brisbane • Singapore • Toronto

This book is printed on acid-free paper.

Library of Congress Cataloging-in-Publication Data:

Polymer Handbook / Editors: J. Brandrup, E. H. Immergut, and E. A. Grulke;
Associate Editors, A. Abe, D. R. Bloch. – 4th ed.
p. cm.
"A Wiley-Interscience Publication."
Includes index.
ISBN 0-471-16628-6 (cloth : alk. paper)
1. Polymers—Tables. 2. Polymerization—Tables. I. Brandrup, J. II. Immergut, E. H. III. Grulke, Eric A.
QD388.P65 1999
547.7–dc21 98-37261

Printed in the United States of America.

10 9 8 7 6 5 4 3 2