Table S1. List of relevant equations and related description for **NRHB** model.

Description	Mathematical expression
S1. Phase equilibrium condition on penetrant chemical potential. The expression for chemical potential is given in a general form which is valid for both pure penetrant ($\phi_1=1$) in the gas phase and for penetrant in the binary polymer mixture.	$$\frac{\mu_1^{GAS}}{RT} = \frac{\mu_1^{POL}}{RT}$$ $$where \quad \frac{\mu_1}{RT} = \ln\frac{\phi_1}{\omega_1 r_1} - r_1\sum_{j=1}^{2}\frac{\phi_j l_j}{r_j} + \ln\tilde{\rho} + r_1(\tilde{v}-1)\ln(1-\tilde{\rho}) - \frac{z}{2}r_1\left[\tilde{v}-1+\frac{q_1}{r_1}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right]$$ $$+ \frac{zq_1}{2}\left[\ln\Gamma_{11} + \frac{r_1}{q_1}(\tilde{v}-1)\ln\Gamma_{00}\right] + r_1\frac{\tilde{P}\tilde{v}}{\tilde{T}} - \frac{q_1}{\tilde{T}_1} + \frac{\mu_{1,H}}{RT}$$ *where* $$\tilde{P} = \frac{P}{P^*}; \quad \tilde{T} = \frac{T}{T^*}; \quad RT^* = P^*v^* = \varepsilon^* \quad with: \varepsilon^* = \sum_{i=1}^{2}\sum_{j=1}^{2}\theta_i\theta_j\varepsilon_{ij}^* \quad v^* = 9.75 cm^3/mol$$ $$\varepsilon_{12}^* = (1-k_{12})\sqrt{\varepsilon_{11}^*\varepsilon_{22}^*}; \quad with \quad \varepsilon_{ii}^* = \varepsilon_{hi}^* + (T-298.15)\varepsilon_{s,i}^*$$ $$\tilde{v} = \frac{V - \sum_{i}^{m}\sum_{j}^{n}N_{ij}V_{ij}^0}{rNv^*} \quad where \ V \ is \ the \ total \ volume \ of \ the \ mixture$$ $$\tilde{\rho} = \frac{1}{\tilde{v}}$$
S2. HB contribution to the expression of chemical potential of penetrant. The expression for the $\mu_{1,H}$ is given in a general form which is valid for both pure penetrant (component 1) in the gas phase and for penetrant in the binary polymer mixture.	$$\frac{\mu_{1,H}}{RT} = r_1\nu_H - \sum_{i}^{m}d_i^1\ln(\frac{v_d^i}{v_{i0}}) - \sum_{j}^{n}a_j^1\ln(\frac{v_a^j}{v_{0j}})$$
S3. Expression of the EOS. The expression for the EOS is given in a general form which is valid for both pure penetrant ($\phi_1=1$) in the	$$\tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) - \tilde{\rho}\left(\sum_{i=1}^{2}\phi_i\frac{l_i}{r_i} - \nu_H\right) - \frac{z}{2}\ln\left(1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right) + \frac{z}{2}\ln\Gamma_{00}\right] = 0$$

gas phase and for penetrant in the binary polymer mixture.	
S4. Average number of hydrogen bonds per molecular segment	$$v_H = \sum_i^m \sum_j^n v_{ij} = \sum_i^m \sum_j^n \frac{N_{ij}}{rN}$$
S5. Expression obtained by minimizing the Gibbs energy as a function of N_{ij} variable.	$$\frac{v_{ij}}{v_{i0}v_{0j}} = \tilde{\rho}\exp(-\frac{G_{ij}^0}{RT})$$ where $$G_{ij}^0 = E_{ij}^0 - T \cdot S_{ij}^0 + p \cdot V_{ij}^0$$
S6. Expression obtained by minimizing the Gibbs energy as a function of the number of contacts between segment of species i and j (0 ,1 and 2 representing, respectively, empty lattice sites, penetrant and polymer)	$$\frac{\Gamma_{ii}\Gamma_{jj}}{\Gamma_{ij}^2} = \exp(-\frac{\Delta\varepsilon_{ij}}{RT})$$ *where* $$\Gamma_{ij} = \frac{N_{ij}^{NR}}{N_{ij}^{NR,0}}$$ *with $N_{ij}^{NR,0}$ representing the effective number of contacts in the compressible lattice between the mers of kind i and the mers of kind j in the case of random statistics.* $$\Delta\varepsilon_{ij} = \varepsilon_{ii} + \varepsilon_{jj} - 2(1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \text{with } \varepsilon_{ii} = \varepsilon_{ii}^*\frac{2}{z}$$
S7. Material balance expression for the non random factors Γs	$$\sum_{i=0}^t \theta_i\theta_r\Gamma_{ij} = 1 \qquad j = 0,1,......, t$$ *where* $$\theta_r = \sum_{i=1}^t \theta_i$$ *Here t is the number of components, '0' representing empty sites.*

S8. Definition of the 'close-packed' specific volume	$v_{sp,i}^* = 1\big/\rho_i^* = v_{sp,0i}^* + (T - 298.15)v_{sp,1i}^*$ *where $v_{sp,1i}^*$ is a characteristic parameters for different homologous series and ρ_i^* is the 'close-packed' density of component 'i'.*

Table S2. List of relevant equations and related description for **NETGP-NRHB** model.

Description	Mathematical expression
S9. Chemical potential of penetrant according to NRHB theory. Expression A4 still holds also in this case. Moreover, due to the hypothesis of 'instantaneous' evolution kinetics for $\underline{N}_{ij}$ and $\underline{N}_{rs}^{NR}$, also eqs. A5, A6 and A7 hold true.	$$\frac{\mu_1^{GAS}}{RT} = \frac{\mu_1^{POL,PE}}{RT}$$ where $$\frac{\mu_1^{GAS}}{RT} =$$ $$\ln\frac{\phi_1}{\delta_1 r_1} - r_1 \sum_{j=1}^{2} \frac{\phi_j l_j}{r_j} + \ln\tilde{\rho} + r_1(\tilde{v}-1)\ln(1-\tilde{\rho}) - \frac{z}{2}r_1\left[\tilde{v}-1+\frac{q_1}{r_1}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right]$$ $$+ \frac{zq_1}{2}\left[\ln\Gamma_{11} + \frac{r_1}{q_1}(\tilde{v}-1)\ln\Gamma_{00}\right] + r_1\frac{\tilde{P}\tilde{v}}{\tilde{T}} - \frac{q_1}{\tilde{T}_1} + \frac{\mu_{1,H}^{GAS}}{RT}$$ $$\frac{\mu_1^{POL,PE}}{RT} =$$ $$\ln\frac{\phi_1}{\delta_1 r_1} - r_1 \sum_{j=1}^{2} \frac{\phi_j l_j}{r_j} + \ln\tilde{\rho} + r_1(\tilde{v}-1)\ln(1-\tilde{\rho}) - \frac{z}{2}r_1\left[\tilde{v}-1+\frac{q_1}{r_1}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] + \frac{zq_1}{2}\left[\ln\Gamma_{11} + \frac{r_1}{q_1}(\tilde{v}-\right.$$ $$-\frac{q_1}{\tilde{T}_1} + \tilde{T}\left[\ln(1-\tilde{\rho}) - \tilde{\rho}\left(\sum_i \phi_i \frac{l_i}{r_i}\right) - \frac{z}{2}\ln\left(1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right) + \frac{z}{2}\ln\Gamma_{00}\right] \cdot \frac{rx_2 \cdot \left.\frac{\partial\tilde{v}}{\partial x_1}\right|_{P,T,\rho_2,\underline{N}_{ij},\underline{N}_{rs}^{NR}}}{\tilde{T}} + \frac{\mu_{1,H}^{POL,PE}}{RT}$$

	where $1/\tilde{v} = \tilde{\rho} = \rho_2 / (\omega_2 \rho^*)$ *according to the hypothesis that $V_{ij}^0 = 0 \quad \forall i,j$; ρ^* represents the close-packed density of polymer-penetrant mixture*
S10. HB contribution to the expression of chemical potential of penetrant in the gas phase.	$$\frac{\mu_{1,H}^{GAS}}{RT} = r_1 v_H - \sum_i^m d_i^1 \ln\left(\frac{v_d^i}{v_{i0}}\right) - \sum_i^m a_j^1 \ln\left(\frac{v_a^j}{v_{0j}}\right)$$
S11. HB contribution to the expression of chemical potential of penetrant in the polymer phase	$$\frac{\mu_{1,H}^{POL,PE}}{RT} = r_1 v_H - \sum_i^m d_i^1 \ln\left(\frac{v_d^i}{v_{i0}}\right) - \sum_j^n a_j^1 \ln\left(\frac{v_a^j}{v_{0j}}\right) + v_H \left.\frac{\partial \ln \tilde{v}}{\partial x_1}\right|_{P,T,\rho_2,\underline{N}_{ij},\underline{N}_{rs}^{NR}} x_2 r$$

Table S3. List of relevant symbols and parameters for **NRHB** and **NETGP-NRHB** models, not explicitly defined in the text..

Description	Symbol *(latin letters)*	Dimension
Number of proton acceptor groups of kind j present on a molecule of type 1	a_j^1	-
Number of proton donor of type i on the molecule of type 1	d_i^1	-
Molar internal energy of formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j	E_{ij}^0	[J mol^{-1}]
Molar Gibbs energy of formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j	G_{ij}^0	[J mol^{-1}]
Mean field lattice fluid binary interactional parameter	k_{12}	-
Dimensionless parameter of component i defined in ref. [46]	l_j	-
Number of types of proton donors	m	-
Number of types of proton acceptors	n	-
Number of occupied cells of the lattice in the mixture or in the pure component	N	-
Number of hydrogen bondings involving a proton donor of type i and a proton acceptor of type j	N_{ij}	-
Characteristic pressure of pure components or average characteristic pressure for the mixture	P^*	[MPa]
Average number of lattice contacts per molecule in the mixture	q	-
Number of lattice contacts per molecule for component 1	q_1	-
Average number of cells occupied per molecule in the mixture	r	-
Lattice cells occupied by one molecule of component 1 in the mixture or in the pure phase of component 1	r_1	-
Lattice cells occupied by one molecule of component 2 in the mixture or in the pure phase of component 2	r_2	-
Universal gas constant	R	[J K^{-1} mol^{-1}]
Molar entropy of formation of hydrogen bonding between the proton donor group of type i and the proton acceptor group of type j	S_{ij}^0	[J mol^{-1}K^{-1}]
Characteristic temperature of pure components or average characteristic temperature for the mixture	T^*	[K]

Description	Symbol	Dimension
Scaled temperature of the mixture	$\tilde{T}$	-
Scaled temperature of the component 1 in pure phase of component 1 or in the mixture	$\tilde{T}_1$	-
'Close-packed' volume of an elementary cell of the lattice in pure components or in the mixture.	$v*$	$[cm^3\ mol^{-1}]$
Temperature independent contribution to 'close-packed' specific volume of the pure component of type 1	$v^*_{sp,01}$	$[cm^3 g^{-1}]$
Temperature independent contribution to 'close-packed' specific volume of the pure component of type 2	$v^*_{sp,02}$	$[cm^3 g^{-1}]$
Scaled lattice fluid volume of the pure components or of the mixture	$\tilde{v}$	-
Molar volume change upon the formation of hydrogen bonding between proton donor group of type i and proton acceptor group of type j	V^0_{ij}	$[cm^3\ mol^{-1}]$
Lattice coordination number	z	-

Description	**Symbol (Greek letters)**	**Dimension**
Non random factor for the distribution of an empty site around another empty site in the lattice	Γ_{00}	-
Non random factor for the distribution of a site occupied by component 1 around another site occupied by component 1 in the lattice	Γ_{11}	-
Number of configurations available to a molecule of component 1 in the 'close-packed' state.	δ_1	-
Lattice fluid interaction energy per mole of contact i-i	ε_{ii}	$[J\ mol^{-1}]$
Average lattice fluid intersegmental interaction energy per mole of average segment in the polymer-water mixture	ε^*	$[J/mol]$
Enthalpic contribution to lattice fluid interaction energy per mole of segment of component 1	ε^*_{h1}	$[J/mol]$
Entropic contribution to lattice fluid interaction energy per mole of segment of component 1	ε^*_{s1}	$[J\ mol^{-1}K^{-1}]$
Enthalpic contribution to lattice fluid interaction energy per mole of segment of component 2	ε^*_{h2}	$[J/mol]$
Entropic contribution to lattice fluid interaction energy per mole of segment of component 2	ε^*_{s2}	$[J\ mol^{-1}K^{-1}]$
Average lattice fluid interaction energy per mole of segment of one molecule	ε^*_{ii}	$[J\ mol^{-1}]$

of component i		
Average lattice fluid interaction energy per mole of average segment in the binary i-j mixture	ε_{ij}^*	[J mol^{-1}]
Surface fraction of component i	θ_i	-
Sum of surface fraction of the component 1 and 2	θ_r	-
Average number of total hydrogen bonds per molecular segment	ν_H	-
Average number of un-bonded proton donor of type i per molecular segment	ν_{i0}	-
Average number of proton donor of type i per molecular segment	ν_d^i	-
Average number of proton acceptor of type j per molecular segment	ν_a^j	-
Average number of un-bonded proton acceptor of type j per molecular segment	ν_{0j}	-
Average number per molecular segment of hydrogen bonding established between a proton donor of type i and a proton acceptor of type j	ν_{ij}	-
'Close packed' density of the polymer-penetrant mixture	ρ^*	[g cm^{-3}]
'Close packed' volumetric fraction of component 1	ϕ_1	-
'Close packed' volumetric fraction of component 2	ϕ_2	-
Mass fraction of component 2	ω_2	-