

Supporting information for:
Time-dependent ATR-FTIR spectroscopic
studies on solvent diffusion and film swelling
in oil paint model systems

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DMA sample composition

Table S1: Overview of the composition of samples for DMA measurements. LO is linseed oil, So is sorbic acid, MSo is either zinc or lead sorbate, So/LO refers to the molar ratio between sorbate molecules (either as free acid or metal complex) and linseed oil, and COOM/COOH refers to the proportion of total sorbate molecules that is bound to a metal ion (either zinc or lead).

sample	LO (mg)	So (mg)	MSo (mg)	So/LO	COOM/COOH
pLO	400	0	0	0	0
Mpol-0	400	30	0	0.6	0
Znpol-32	400	20	12.8	0.6	0.32
Znpol-64	400	10	25.6	0.6	0.64
Znpol-100	400	0	38.4	0.6	1.00
Znpol-std.	400	0	57.1	0.2	1.00
Pbpol-32	400	20	19.2	0.6	0.32
Pbpol-64	400	10	38.3	0.6	0.64
Pbpol-100	400	0	57.5	0.6	1.00
Pbpol-std.	400	0	84.9	0.2	1.00

Peak fit procedure for DMA

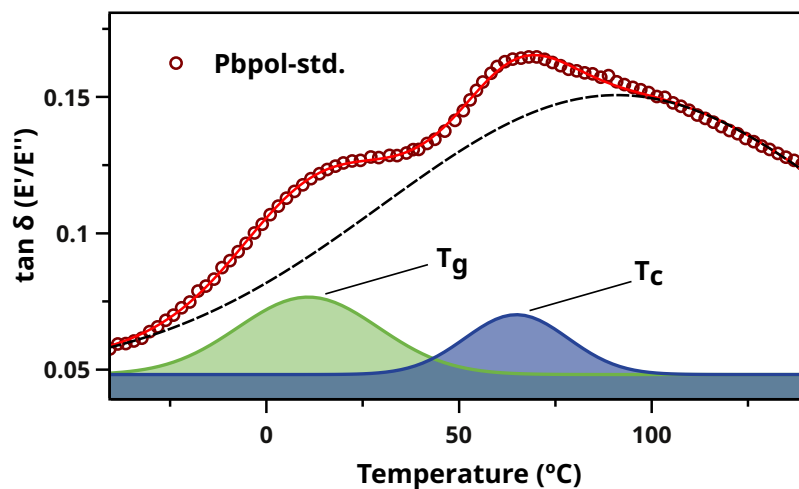


Figure S1: Illustration of fitting procedure to obtain both T_g and T_c . The total signal intensity (red curve) is a summation of three Gaussian functions. The black dashed curve is one of the three Gaussian functions that is fitted to the experimental data, and serves as a background. The green (T_g) and blue (T_c) functions correspond to the signals for the bulk glass transition and cluster glass transition, respectively.

FTIR spectra showing characteristic solvent bands

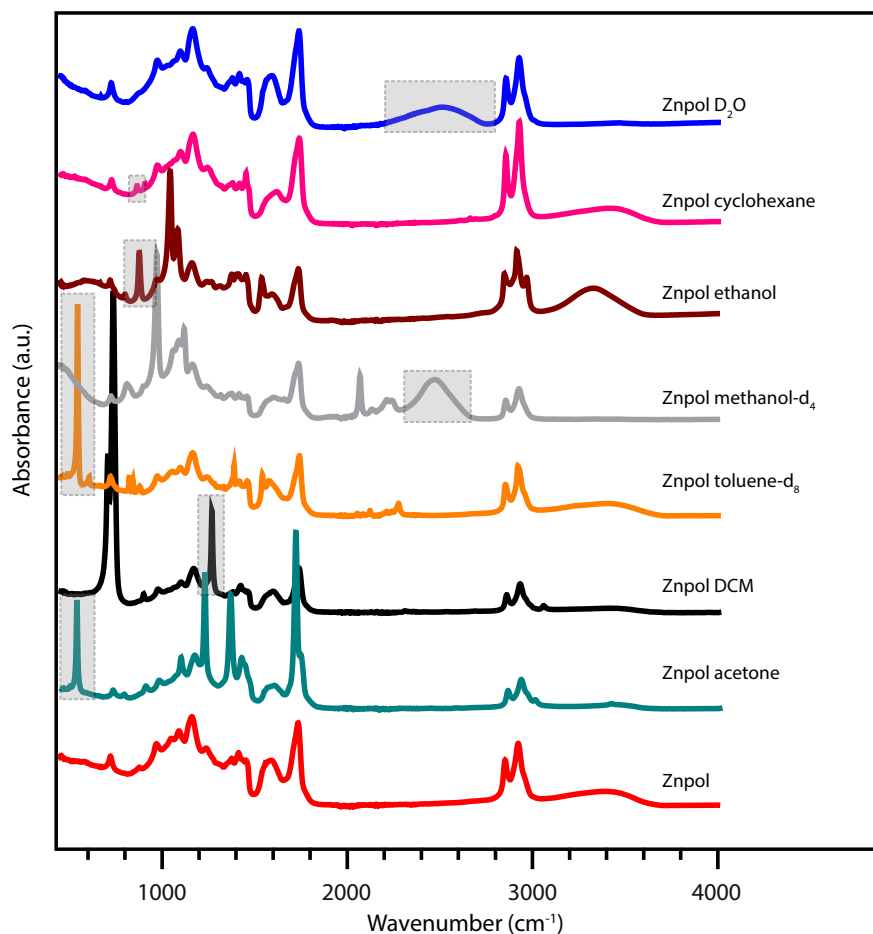


Figure S2: FTIR spectra of Zn pol ionomer samples saturated with each of the investigated solvents. Dashed boxes indicate the characteristic solvent band that was integrated and used to follow solvent diffusion over time.

Storage modulus plots

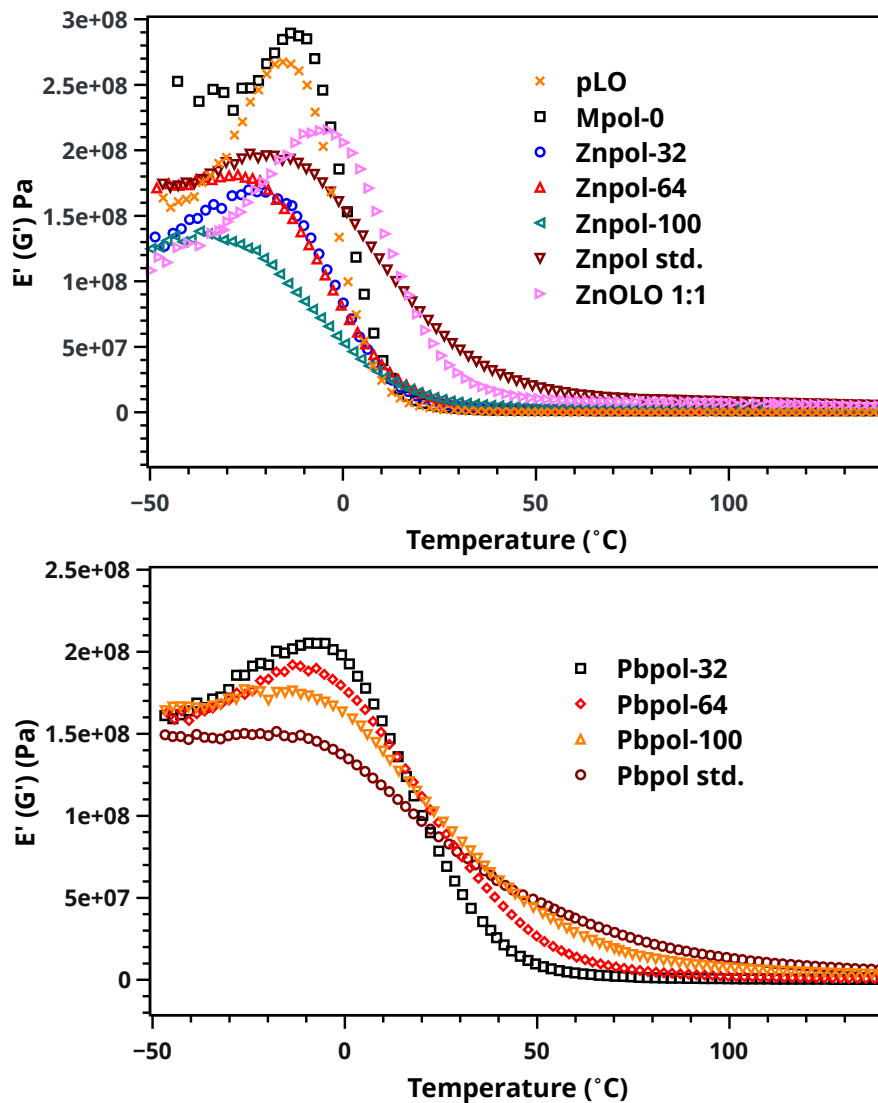


Figure S3: Storage modulus (E') values over the temperature range -50–140 $^{\circ}\text{C}$. Rubbery plateau region was defined at 140 $^{\circ}\text{C}$.

Fickian diffusion profile fits, with and without τ_d

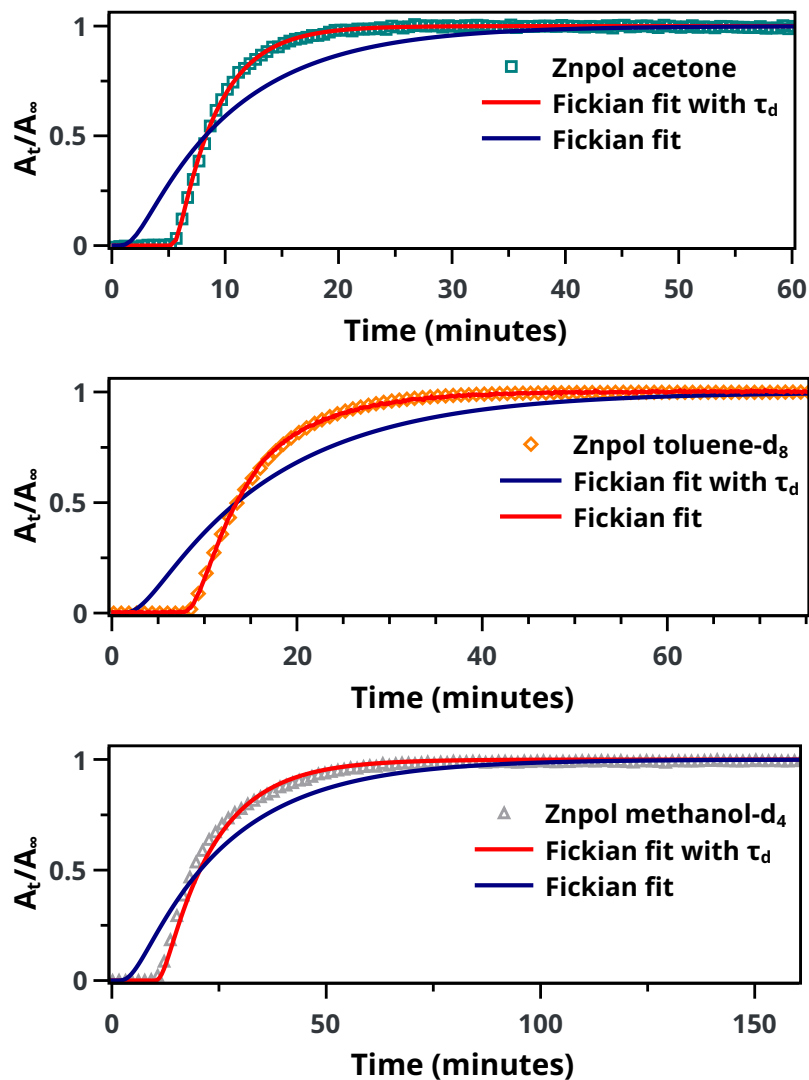


Figure S4: Concentration profile for acetone, toluene- d_8 and methanol- d_4 in **Znpol** using a standard (blue) and adapted (red) Fickian diffusion model to fit the data. The standard Fickian model clearly does not predict the delay time τ_d .

Table of D_{Fick} values

Table S2: Fitted values for parameter D_{Fick} using the adapted Fickian model according to Eq. 3. The error in D_{Fick} values corresponds to the 95% confidence interval.

Solvent	Znpol D_{Fick} (m ² /s)	Pbpol D_{Fick} (m ² /s)	ZnO-LO D_{Fick} (m ² /s)
DCM	$1.4 \times 10^{-10} \pm 0.04$	$1.4 \times 10^{-10} \pm 0.04$	$1.6 \times 10^{-10} \pm 0.05$
acetone	$5.6 \times 10^{-11} \pm 0.1$	$6.1 \times 10^{-11} \pm 0.2$	$7.5 \times 10^{-11} \pm 0.2$
toluene- d_8	$2.5 \times 10^{-11} \pm 0.04$	$3.1 \times 10^{-11} \pm 0.04$	$2.2 \times 10^{-11} \pm 0.06$
methanol- d_4	$1.0 \times 10^{-11} \pm 0.02$	$7.2 \times 10^{-12} \pm 0.1$	$1.5 \times 10^{-11} \pm 0.03$
ethanol	$4.3 \times 10^{-12} \pm 0.05$	$4.0 \times 10^{-12} \pm 0.05$	$5.0 \times 10^{-12} \pm 0.07$
cyclohexane	$1.4 \times 10^{-12} \pm 0.01$	$1.1 \times 10^{-12} \pm 0.06$	$5.2 \times 10^{-13} \pm 0.04$
D ₂ O	$6.1 \times 10^{-13} \pm 0.01$	$5.3 \times 10^{-13} \pm 0.04$	$3.5 \times 10^{-13} \pm 0.03$

Table of D_{eq} values

Table S3: Fitted values for parameter D_{eq} using the diffusion-swelling model according to Eq. 6. The error in D_{eq} values corresponds to the 95% confidence interval.

Solvent	Znpol D_{eq} (m ² /s)	Pbpol D_{eq} (m ² /s)	ZnO-LO D_{eq} (m ² /s)
DCM	$66 \times 10^{-11} \pm 16$	$55 \times 10^{-11} \pm 14$	$38 \times 10^{-11} \pm 15$
acetone	$15 \times 10^{-11} \pm 4$	$23 \times 10^{-11} \pm 8$	$17 \times 10^{-11} \pm 5$
toluene- d_8	$8.7 \times 10^{-11} \pm 2$	$9.9 \times 10^{-11} \pm 2$	$3.7 \times 10^{-11} \pm 1$
methanol- d_4	$5.4 \times 10^{-11} \pm 1$	$2.3 \times 10^{-11} \pm 0.6$	$2.3 \times 10^{-11} \pm 0.7$
ethanol	$1.9 \times 10^{-11} \pm 0.4$	$1.6 \times 10^{-11} \pm 0.4$	$1.2 \times 10^{-11} \pm 0.3$
cyclohexane	$2.7 \times 10^{-12} \pm 0.9$	$3.0 \times 10^{-12} \pm 0.7$	$8.6 \times 10^{-13} \pm 3$
D ₂ O	$5.1 \times 10^{-13} \pm 2$	$6.4 \times 10^{-13} \pm 2$	$3.8 \times 10^{-13} \pm 1$

Table of α values

Table S4: Fitted values for parameter α using the diffusion-swelling model according to Eq. 6. The error in α values corresponds to the 95% confidence interval.

Solvent	Zn α	Pb α	ZnO-LO
DCM	-8.0 ± 0.8	-8.90 ± 0.79	-7.4 ± 1.6
acetone	-9.6 ± 1.5	-9.2 ± 1.3	-10.6 ± 3.0
toluene- d_8	-10.5 ± 1.6	-13.3 ± 1.8	-12.9 ± 7.5
methanol- d_4	-7.5 ± 0.6	-9.4 ± 1.4	-12.7 ± 7.7
ethanol	-7.6 ± 0.6	-8.00 ± 0.63	-7.3 ± 1.8
cyclohexane	-19.2 ± 9.1	-10.5 ± 1.6	-12.2 ± 7.3
D $_2$ O	0	-6.6 ± 4.4	0

Table of solvent properties

Table S5: Pure solvent properties.^{S1}

solvent	D_{self} (m ² /s)	radius (Å)	density (kg/m ³)	M_W (g/mol)
DCM	3.5×10^{-9}	4.30	1330	84.9
acetone	1.3×10^{-9}	4.55	790	58.1
toluene- <i>d</i> ₈	2.2×10^{-9}	5.38	943	100
methanol- <i>d</i> ₄	5.9×10^{-9}	3.54	888	36.0
ethanol	2.8×10^{-9}	4.18	790	46.0
cyclohexane	3.8×10^{-9}	5.48	776	84.1
D ₂ O	5.5×10^{-9}	2.74	1100	20

Relation between D and the polymer fraction

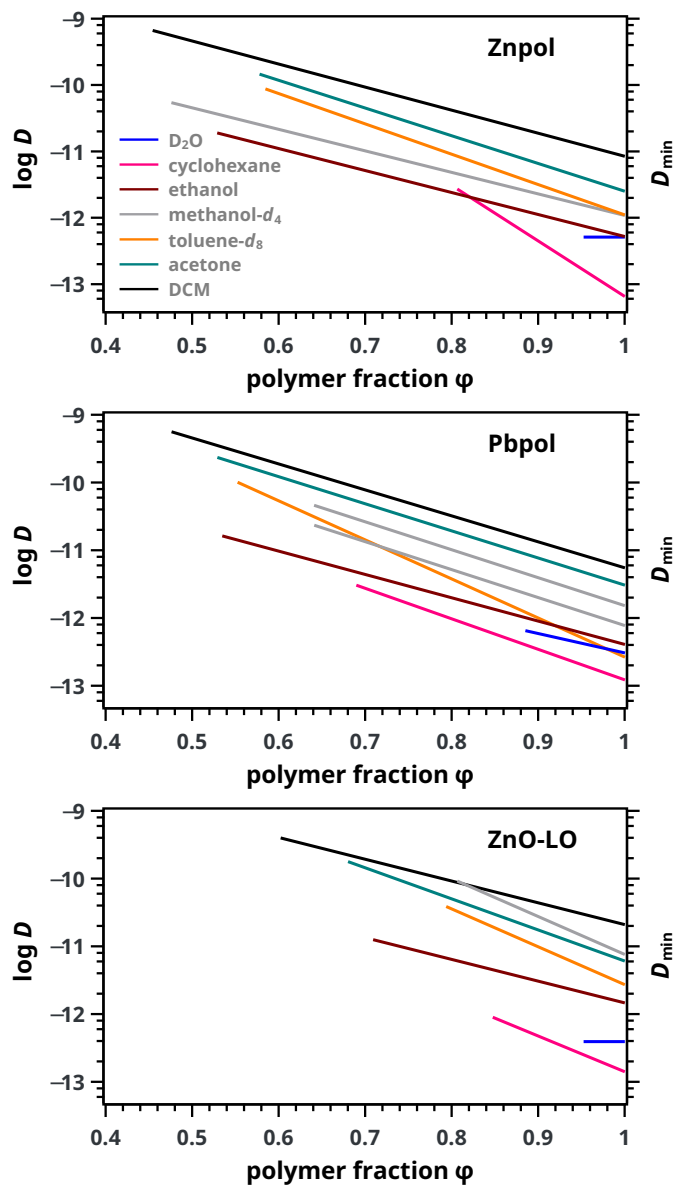


Figure S5: Diffusion coefficient in **Zn-pol**, **Pb-pol** and **ZnO-LO** film versus polymer fraction ϕ , calculated using the diffusion-swelling model, Eq. 7, using parameters in Tables S3 and S4.

Correlation between D_{Fick} and D_{eq}

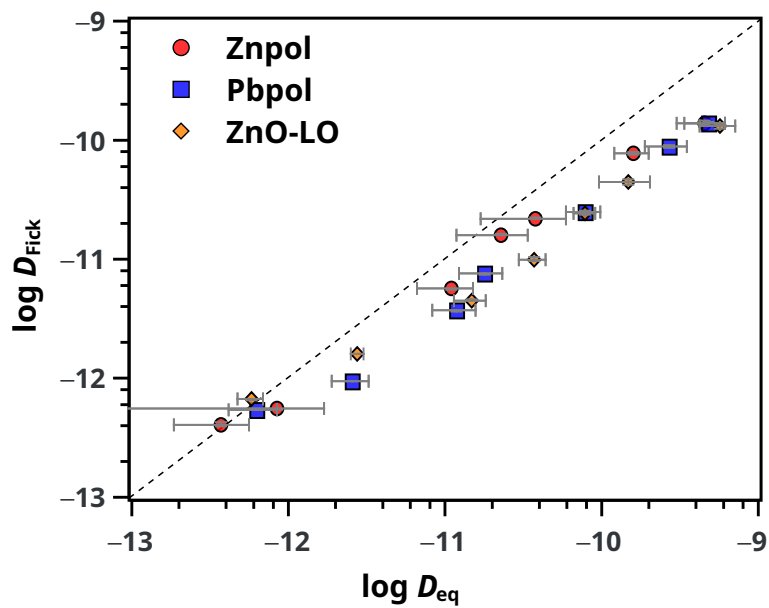


Figure S6: Correlation between diffusion coefficient assuming Fickian diffusion (D_{Fick}) and diffusion coefficient at equilibrium swelling (D_{eq}) calculated using the diffusion-swelling model.

Relation between α and the solvent molecule radius

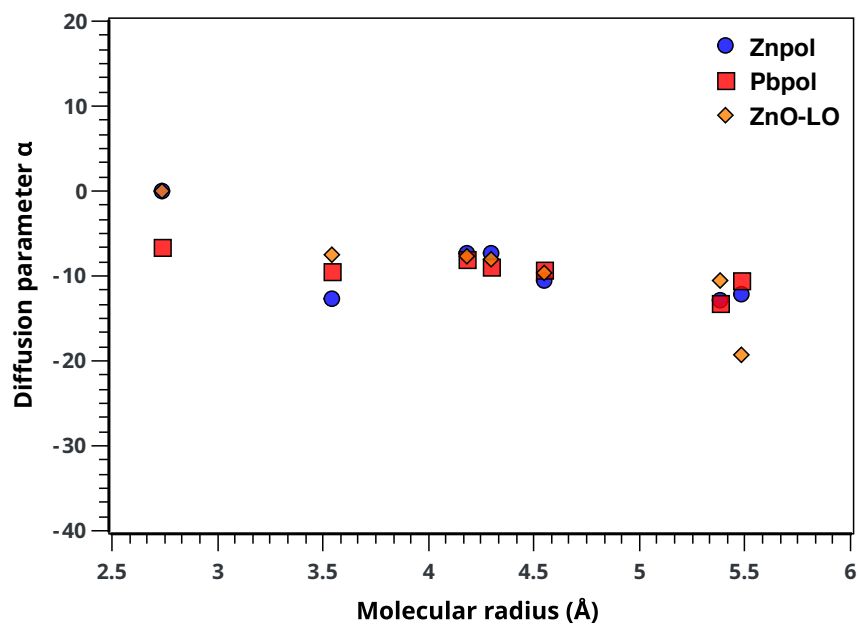


Figure S7: Correlation between parameter α in the diffusion-swelling model with molecular radius of the solvent.

Relation between D and dynamic viscosity

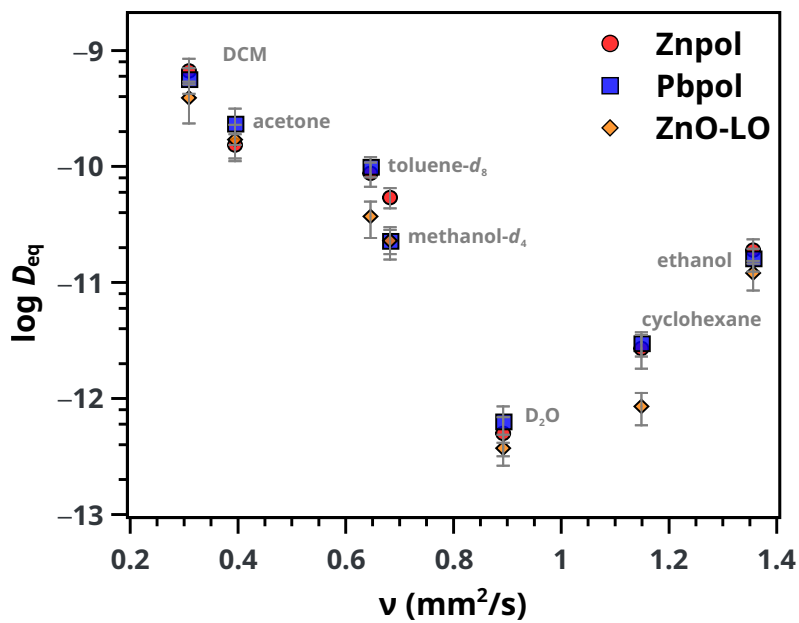


Figure S8: The relation between the measured diffusion coefficients in Znpol for the investigated set of solvents (plotted as the natural logarithm for clarity) versus their kinematic viscosity values ν (dynamic viscosity η divided by density ρ). Kinematic viscosity values are at 298 K and taken from Ref.^{S1}.

Parameter estimation procedure

The model described in the main text is employed in the parameter estimation procedure to find the diffusion parameters, D_{eq} and α . The procedure could be performed using a direct optimization procedure as the number of parameters to be estimated is small. The cost function, $C(\bar{D}, \alpha)$, was constructed on the basis of the values of the concentration curves from the solvent FTIR band areas, c_i , and the model predicted values, \hat{c}_i , on the same instants of time, t_i , over the time interval, where the concentration changes are appreciable:

$$C(\bar{D}, \alpha) = \sum_{i=1}^N (c_i - \hat{c}_i(\bar{D}, \alpha))^2 \quad (1)$$

Here, N denotes the number of time point of concentration data for each solvent/polymer sample.

Although the optimization procedure has provided a set of parameters that allow a good description of the experimental data, yet some of the parameters could still be correlated. The estimability of such correlated parameters is problematic, they would have large error or even turn out to be completely inestimable. Therefore, we have applied a method to calculate the 95% confidence intervals of the parameters using a least squares procedure^{S2} based on a linearization of the non-linear kinetic model at parameter values listed in Table S3 and S4. This method requires to calculate the sensitivity matrix \mathbf{X} containing the partial derivatives of the observable c_i , to the parameters, D_{eq} and α :

$$\mathbf{X} = \begin{bmatrix} \frac{1}{\sigma_c} \frac{\partial c_1}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_1}{\partial \alpha} \\ \frac{1}{\sigma_c} \frac{\partial c_2}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_2}{\partial \alpha} \\ \vdots & \vdots \\ \frac{1}{\sigma_c} \frac{\partial c_N}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_N}{\partial \alpha} \end{bmatrix} \quad (2)$$

Here, the $\frac{1}{\sigma_c} \frac{\partial c_i}{\partial \bar{D}}$ and $\frac{1}{\sigma_c} \frac{\partial c_i}{\partial \alpha}$ denote the partial derivatives of concentration for each measurement point i to the parameters D_{eq} and α , respectively. Note that the number of rows in

X equals N , the number of time point of concentration data for each solvent/polymer sample. The parameter sensitivities are numerically computed from the diffusion model and subsequently scaled with the standard deviation of concentration measurements, σ_c . The vector of standard deviations of the estimated parameters D_{eq} and α , follows as:

$$\begin{bmatrix} s_{\bar{D}} & s_{\alpha} \end{bmatrix} = \sqrt{(\mathbf{X}^T \mathbf{X})^{-1}} \quad (3)$$

The 95% confidence interval is calculated from this standard deviation as:

$$\begin{bmatrix} s_{\bar{D}} & s_{\alpha} \end{bmatrix}_{95} = 1.96 \begin{bmatrix} s_{\bar{D}} & s_{\alpha} \end{bmatrix} \quad (4)$$

The value for the standard deviation of the concentration, σ_c , is obtained from 9 repeated measurements of the relative concentration curves for acetone in **ZnPol**. One value was obtained by simply constructing an average curve from the set of 9 curves and determining the standard deviation as the sum of the squared differences at each time point of the individual curves with the average curve:

$$\sigma_c = \sum_{j=1}^9 \sqrt{\frac{1}{N} \sum_{i=1}^N (c_i - \bar{c}_i)^2} \quad (5)$$

Here, i counts the N time points ($N = 33$) at the interval, where the concentration changes appreciably, while c_i and \bar{c}_i are the values of the measured and average concentrations at time points t_i . The value thus obtained was $\sigma_c = 0.087$. However, the equilibrium swelling factor and film thicknesses measured for these 9 samples are not the same, so part of the standard deviation calculated this way must be attributed to differences in swelling factor and thickness. Therefore, we decided to employ a different method to estimate σ_c , where we use the diffusion model to account for the differences in swelling factor and thickness. Using a similar cost function as Eq. 1 and minimizing this we obtained the best fit values for D_{eq} and α for all the 9 acetone/**ZnPol** series at the measured time points:

\hat{c}_i . Replacing \bar{c}_i by \hat{c}_i in Eq. / 3 now leads to a σ_c value corrected for swelling factor and thickness, which turned out to be $\sigma_c = 0.047$. The fact that this value is smaller is an indication indeed that part of the deviations between the 9 curves must be ascribed to differences in swelling factor and thickness. We decided that the lower estimate of σ_c is the proper value to calculate the scaled matrix \mathbf{X} .

However, it is not sufficient to account for the error in concentration only, since the measured values of both the swelling factor and the film thickness are used, via the diffusion model, to determine the diffusion parameters, do also contain considerable error. We have determined the standard deviation of thickness, σ_δ , by measuring it repeatedly at different places on one film sample, which yielded $\sigma_\delta \approx 10^{-5}$ m. The standard deviation of the swelling factor, σ_f , as measured by the FTIR polymer band area, was obtained from the 9 acetone/**ZnPol** samples also used to estimate σ_c . Thus, σ_f turned out to be 0.13 (swelling factors are between 1 and 2.5). When determining the errors in the diffusion parameters using the sensitivity matrix, we could account for the errors in thickness and swelling factor in an elegant way by treating them as both *parameters* and *measurements* at the same time. This implies, in the first place, that we have to extend the optimization problem with two additional parameters: thickness δ and equilibrium swelling factor f . Consequently, the starting values for these parameters of the constraint optimization problem are set equal to their measured values, δ and f , and their constraints at $\delta \pm \sigma_\delta$ and $f \pm \sigma_f$, respectively. The second implication of treating δ and f as both parameters and measurements implies that sensitivity matrix \mathbf{X} has two more columns and also two more rows. The extra columns denote the sensitivities of concentration to parameter thickness, δ , and to equilibrium swelling factor, f , while the extra two rows refer to the measurements sensitivity to the parameter. As for these rows the parameters are identical to the measurements, the unscaled elements on the diagonal are just ones, as obviously $\frac{\partial \delta}{\partial \delta} = 1$ and $\frac{\partial f}{\partial f} = 1$. Since scaling by the standard deviation is required, the ultimate values of these elements become $1/\sigma_\delta$ and $1/\sigma_f$, respectively (and zeros in non-diagonal

positions). Thus, we obtain an extended \mathbf{X} matrix:

$$\mathbf{X} = \begin{bmatrix} \frac{1}{\sigma_c} \frac{\partial c_1}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_1}{\partial \alpha} & \frac{1}{\sigma_c} \frac{\partial c_1}{\partial \delta} & \frac{1}{\sigma_c} \frac{\partial c_1}{\partial f} \\ \frac{1}{\sigma_c} \frac{\partial c_2}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_2}{\partial \alpha} & \frac{1}{\sigma_c} \frac{\partial c_2}{\partial \delta} & \frac{1}{\sigma_c} \frac{\partial c_2}{\partial f} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{1}{\sigma_c} \frac{\partial c_N}{\partial \bar{D}} & \frac{1}{\sigma_c} \frac{\partial c_N}{\partial \alpha} & \frac{1}{\sigma_c} \frac{\partial c_N}{\partial \delta} & \frac{1}{\sigma_c} \frac{\partial c_N}{\partial f} \\ 0 & 0 & \frac{1}{\sigma_\delta} & 0 \\ 0 & 0 & 0 & \frac{1}{\sigma_f} \end{bmatrix} \quad (6)$$

We also obtain two more standard deviations from (cf. Eq. 3):

$$\begin{bmatrix} s_{\bar{D}} & s_\alpha & s_\delta & s_f \end{bmatrix} = \sqrt{(\mathbf{X}^T \mathbf{X})^{-1}} \quad (7)$$

We have used the extended sensitivity matrix \mathbf{X} to estimate the 95% confidence intervals of D_{Fick} , D_{eq} and α listed in Table S2, S3 and S4. It was noted that their values were significantly increased by mostly the error in the equilibrium swelling factor. Furthermore, treating δ and f as both parameters and measurements allowed optimization of δ and f as well, but in only two cases this procedure yielded slightly different values for the swelling factor than the measured ones.

References

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- (S2) Yao, K. Z.; Shaw, B. M.; Kou, B.; McAuley, K. B.; Bacon, D. W. Modeling Ethylene/Butene Copolymerization with Multi-site Catalysts: Parameter Estimability and Experimental Design. *Polymer Reaction Engineering* **2003**, *11*, 563–588.