Influence of resins on the structure and dynamics of SBR compounds: a Solid-State NMR study

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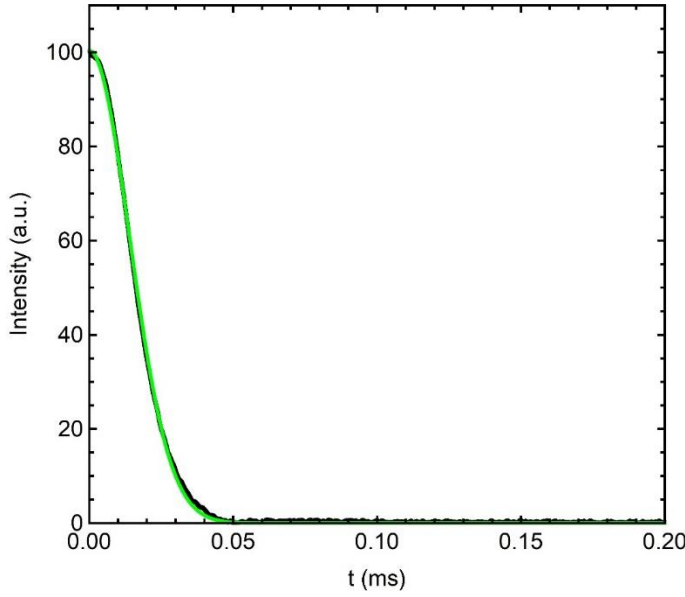
SUPPLEMENTARY MATERIAL

Figure S1. [1]H FID (black points) and Gaussian fitting function (green line) obtained for Kristalex.

[1]H-^{13}C CP Dynamics

The [1]H-^{13}C CP dynamics was studied at 303 K for Kristalex, vSBR and vSBR_k by acquiring spectra at different contact time values (τ_{CP}) and measuring the integral intensity ($I(\tau_{CP})$) of specific signals. In particular, for Kristalex and vSBR_k, the integral of the most intense sideband of the aromatic tertiary carbons of the resin (from 157 to 180 ppm) was considered in the analysis, whereas, for vSBR, the integral of the region of aromatic/alkene carbons (from 100 to 155 ppm) was taken. The $I(\tau_{CP})$ curves of vSBR and vSBR_k were fitted according to equation S1:

$$I(\tau_{CP}) = I_0 \frac{1}{1 - T_{CH}/T_{1\rho}} \left(e^{-\frac{\tau_{CP}}{T_{1\rho}}} - e^{-\frac{\tau_{CP}}{T_{CH}}} \right) \tag{S1}$$

with T_{CH} being the rate constant for the polarization transfer process and $T_{1\rho}$ the spin-lattice relaxation time in the rotating frame of ^{1}H nuclei.

In the case of Kristalex, the $I(\tau_{CP})$ curves were fitted according to equation S2:

$$I(\tau_{CP}) = I_0 \frac{1}{1 - T_{CH}/T_{1\rho}} \left(e^{-\frac{\tau_{CP}}{T_{1\rho}}} - e^{-\left(\frac{\tau_{CP}}{T_{CH}}\right)^{\beta}} \right) \tag{S2}$$

with $0 < \beta \leq 1$, taking into account a distribution of T_{CH} values. For this sample, β was found to be 0.3.

The results of the fittings are shown in Figure S2; T_{CH} and $T_{1\rho}$ values obtained from the analysis are reported in Table S1.
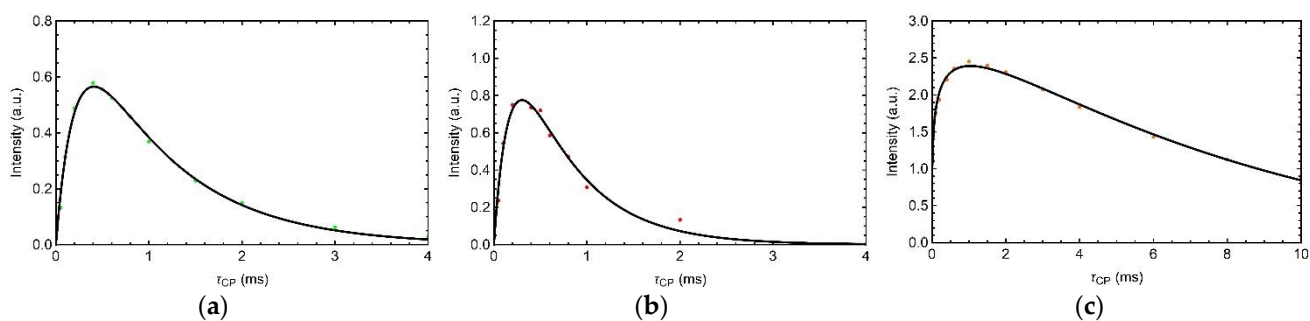
Figure S2. Integral intensities of the ¹³C CP/MAS signals (points) and fitting functions (black lines) obtained for vSBR (**a**), vSBR_k (**b**) and Kristalex (**c**) as a function of the contact time τ_{CP}.

Table S1. T_{CH} and $T_{1\rho}$ values obtained from the analysis of the CP curves for the investigated samples.

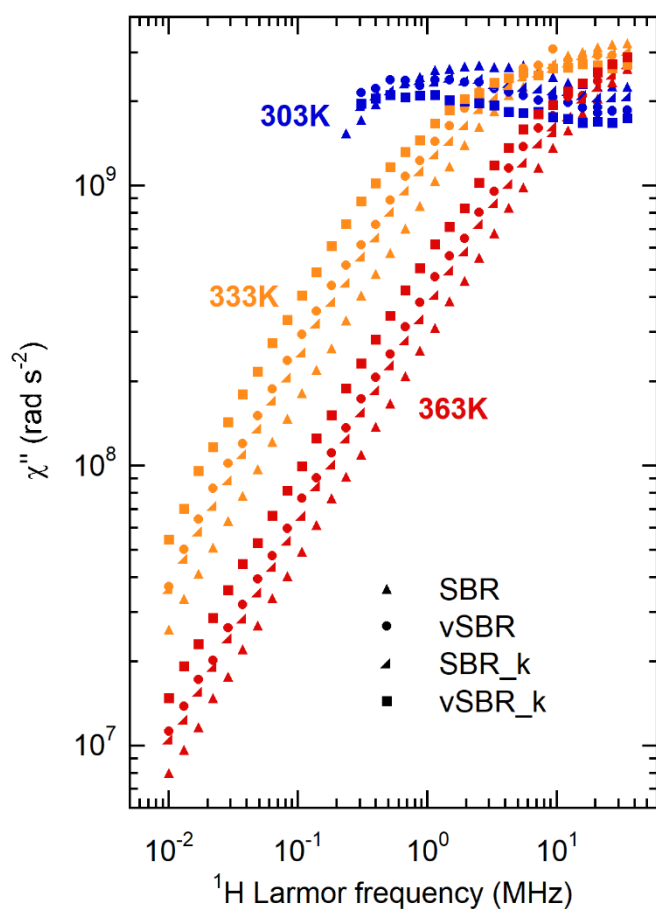| Sample	T_{CH} (ms)	$T_{1\rho}$ (ms)
vSBR	0.2	1.0
vSBR_k	0.2	0.6
Kristalex	0.7	8.6

Figure S3. ¹H NMR susceptibility curves of the investigated samples at the indicated temperatures.

Table S2. [1]H $T_{1\varrho,i}$ values and relative weight percentages (W_i) obtained for vSBR and vSBR_k at the investigated temperatures. Errors are ± 1 on the last digit.

vSBR					vSBR_k				
T (K)	W_a (%)	W_b (%)	$T_{1\varrho,a}$ (ms)	$T_{1\varrho,b}$ (ms)	T (K)	W_a (%)	W_b (%)	$T_{1\varrho,a}$ (ms)	$T_{1\varrho,b}$ (ms)
303	83	17	0.7	4.4	303	87	13	0.6	4.9
313	73	27	0.9	5.0	313	79	21	0.7	4.4
323	64	36	1.3	6.6	323	70	30	1.0	5.1
333	53	47	1.7	8.7	333	60	40	1.3	6.6
343	43	57	2.3	11.0	343	50	50	1.6	8.4

Table S3. [1]H $R_{1\rho}^{PWRA}$ (experimental), $R_{1\rho}^{seg}$ (calculated) and $R_{1\rho}^{pol}$ (calculated) obtained for vSBR and vSBR_k at the investigated temperatures.

vSBR				vSBR_k			
T (K)	$R_{1\rho}^{PWRA}$ (s[-1])	$R_{1\rho}^{seg}$ (s[-1])	$R_{1\rho}^{pol}$ (s[-1])	T (K)	$R_{1\rho}^{PWRA}$ (s[-1])	$R_{1\rho}^{seg}$ (s[-1])	$R_{1\rho}^{pol}$ (s[-1])
303	1257	658	599	303	1388	732	656
313	869	292	577	313	1115	378	737
323	559	137	422	323	783	195	588
333	360	67	293	333	521	101	420
343	240	34	206	343	367	52	315