SUPPORTING INFORMATION

Preparation and dielectric properties of poly(acrylonitrile-co-2,2,2-trifluoroethyl methacrylate) materials via radical emulsion copolymerization

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**IR spectroscopy**

All FTIR spectra of the copolymers show the characteristic bands of both comonomers incorporated in the copolymers. Figure S1 displays the IR spectrum of poly(AN-co-MATRIF) copolymer prepared from a feed molar ratio of [AN]<sub>0</sub>:[MATRIF]<sub>0</sub> =50:50 (Entry E3, Table 1). It reveals the characteristic bands at 2989 cm<sup>-1</sup> (aliphatic CH), 2243 cm<sup>-1</sup>(CN), 1754 cm<sup>-1</sup>(C=O), 1287 cm<sup>-1</sup> (aliphatic C-F) and 1169-1128 cm<sup>-1</sup> (C-O). In addition, the bands at 655 and 974 cm<sup>-1</sup> are attributed to the bending vibrations of C-F and C-H, respectively.

![Fig. S1 FTIR Spectrum of P(AN-co-MATRIF) copolymer (Entry E3, Table 1)](image)
Figure S2: $^1$H NMR spectra of homopolymers and copolymers: (a) P(MATRIF), (b) P(AN-co-MATRIF) 75/25; (c) P(AN-co-MATRIF) 25/75; (d) P(AN-co-MATRIF) 50/50; (e) P(AN-co-MATRIF) 85/15, and (f) Poly(AN) (Entries: E1-E4, Table 1) recorded in DMF-d$_7$ at RT. The stared signals represents the DMF signals.
**Kinetics of radical emulsion copolymerization of AN and MATRIF monomers at high conversion**

**Model**

Monomer reactivity ratios are interesting parameters to predict the copolymer composition. The model of Extended Kelen-Tüdos \(^1\-^4\) was applied to assess the reactivity ratios of AN \((r_1)\) and MATRIF \((r_2)\). The Extended Kelen-Tüdos model is based on the following equation:

\[
\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_1}{\alpha}
\]

where \(\eta = \frac{G}{H + \alpha}\) and \(\xi = \frac{H}{H + \alpha}\)

and \(\alpha = \sqrt{H_{\text{min}}H_{\text{max}}}\)

\(H_{\text{min}}\) and \(H_{\text{max}}\) correspond to the lowest and the highest values of \(H\).

\(H\) and \(G\)

\[
H = \frac{Y}{Z^2} \quad \text{and} \quad G = \frac{(Y-1)}{Z}
\]

With

\[
Z = \frac{\log(1-\xi)}{\log(1-\xi)}
\]

Where \(\xi_1 = \xi_1\left(\frac{Y}{X}\right)\) and \(\xi_2 = \xi_2\left(\frac{\mu + X}{\mu + Y}\right)\)

\(X = \frac{f_1}{f_2}\) and \(Y = \frac{F_1}{F_2}\)

\(f_1, f_2, F_1\) and \(F_2\) represent the AN and MATRIF molar fractions in the feed determined from the monomers ratio, and these in the copolymer determined by \(^1\text{H NMR}\), respectively.

\(W\) is the weight conversion of the polymerization after purification (yield (wt. %)) and \(\mu\) is the ratio between the molar mass of MATRIF and AN.

**Validity limit of EKT model**

This method has the potential to be used for weight conversion (yield) up to 40%. For other authors, this model can fit the experimental data above 40% as weight conversion such as study reported by v et al.,\(^3\) where the weight conversion is ranging between 24 and 60% when EKT model was used. Indeed, the kinetics of the radical copolymerization of MATRIF with tert-butyl \(\alpha\)-trifluoromethacrylate was published by our group.\(^4\) It was performed in Carius tubes, initiated by tert-butyl-peroxypivalate for 14 h at 74 °C by varying the ratio of both comonomers in the feed. The copolymers were purified by removing the monomers, then weighed to assess
the weight conversion (Z). The reactivity ratios were determined using the EKT model which
fit the experimental points, the yield were ranging between 11% and 80%. In this EKT model
described in our manuscript, Z, ranged between 54 and 62%, is the weight conversion (%wt
yield) obtained after purification of the copolymer (and not the molar conversion of monomers
as used in the classical FR and KT models at low conversion using crude product).

Table S1

Extended Kelen-Tüdos parameters for P(AN-co-MATRIF) copolymers for high
conversion prepared by radical emulsion copolymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Y</th>
<th>X</th>
<th>ξ₂</th>
<th>ξ₁</th>
<th>Z</th>
<th>G</th>
<th>H</th>
<th>ξ</th>
<th>η</th>
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<tr>
<td>E1</td>
<td>0.235</td>
<td>0.176</td>
<td>0.570</td>
<td>0.758</td>
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<td>-0.456</td>
<td>0.083</td>
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<tr>
<td>E2</td>
<td>0.389</td>
<td>0.333</td>
<td>0.532</td>
<td>0.620</td>
<td>1.276</td>
<td>-0.479</td>
<td>0.239</td>
<td>0.0777</td>
<td>-0.1558</td>
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<tr>
<td>E3</td>
<td>0.786</td>
<td>1.000</td>
<td>0.633</td>
<td>0.497</td>
<td>0.686</td>
<td>-0.312</td>
<td>1.668</td>
<td>0.3706</td>
<td>-0.0646</td>
</tr>
<tr>
<td>E4</td>
<td>1.500</td>
<td>3.000</td>
<td>0.819</td>
<td>0.410</td>
<td>0.308</td>
<td>1.623</td>
<td>15.799</td>
<td>0.8481</td>
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<tr>
<td>E5</td>
<td>1.941</td>
<td>5.667</td>
<td>0.934</td>
<td>0.320</td>
<td>0.142</td>
<td>6.623</td>
<td>96.132</td>
<td>0.9715</td>
<td>0.0667</td>
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</table>

References


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