

### Electronic Supplementary Information

**Table S1.** Copolymerization data for classic approach obtained from on-line <sup>1</sup>H-NMR kinetic experiments for free radical solution copolymerization of VAc/DBM system at 60°C

$f_{VAc}(t)$	$F_{VAc}(\Delta t')$	$x(\Delta t')$
<b>VD1</b>		
0.7143	0.5660	0.0755
0.7143	0.5849	0.1176
0.7143	0.6096	0.3482
0.7143	0.6114	0.3673
0.7143	0.6163	0.4241
0.7143	0.6143	0.4381
0.7143	0.6126	0.4534
0.7143	0.6162	0.4750
<b>VD2</b>		
0.8333	0.6622	0.0590
0.8333	0.6646	0.1204
0.8333	0.6515	0.1654
0.8333	0.6770	0.2394
0.8333	0.6725	0.2582
0.8333	0.6784	0.2804
0.8333	0.6932	0.3256
0.8333	0.6896	0.3517
0.8333	0.6880	0.3669
0.8333	0.6899	0.3807
0.8333	0.6991	0.4005
0.8333	0.7048	0.4304
0.8333	0.7040	0.4409
0.8333	0.7131	0.4584
0.8333	0.7076	0.4673
0.8333	0.7144	0.4802

**Table S2.** Copolymerization data for new approach obtained from on-line  $^1\text{H-NMR}$  kinetic experiments spectra at different reaction time intervals up to medium overall monomer conversion for free radical solution copolymerization of VAc/DBM system at  $60^\circ\text{C}$

VD1					
$f_{VAc}(t)$	$F_{VAc}(\Delta t')$	$x(\Delta t')$	$f_{VAc}(t)$	$F_{VAc}(\Delta t')$	$x(\Delta t')$
0.7268	0.5565	0.0109	0.7561	0.6345	0.1210
0.7287	0.6205	0.0590	0.7561	0.6150	0.1463
0.7287	0.5975	0.0489	0.7561	0.6345	0.1803
0.7290	0.5678	0.0164	0.7648	0.6207	0.0972
0.7290	0.5608	0.0371	0.7648	0.6243	0.1492
0.7290	0.6096	0.0638	0.7648	0.6281	0.1686
0.7304	0.5842	0.0660	0.7681	0.6167	0.0745
0.7317	0.6171	0.0924	0.7681	0.6226	0.1278
0.7317	0.6182	0.1125	0.7681	0.6273	0.1477
0.7329	0.5947	0.0300	0.7729	0.6344	0.0674
0.7329	0.6036	0.0750	0.7729	0.6393	0.1558
0.7329	0.6078	0.0955	0.7729	0.6401	0.1821
0.7355	0.5913	0.1100	0.7803	0.6310	0.0575
0.7371	0.6095	0.0465	0.7803	0.6381	0.0791
0.7371	0.6137	0.0675	0.7829	0.6430	0.0948
0.7371	0.5622	0.0846	0.7829	0.6435	0.1229
0.7371	0.6246	0.1321	0.7829	0.6444	0.1508
0.7407	0.5768	0.0765	0.7829	0.6381	0.1790
0.7407	0.5984	0.0980	0.7975	0.6451	0.0311
0.7434	0.6230	0.0221	0.7975	0.6466	0.0618
0.7543	0.6266	0.0764	0.7975	0.6326	0.0930
0.7543	0.6234	0.1662	0.8024	0.6481	0.0317
0.7561	0.6052	0.0544	0.8024	0.6263	0.0639
0.7561	0.6134	0.0775	0.8075	0.6048	0.0333

Table S2. Continued

VD2					
$f_{VAc}(t)$	$F_{VAc}(\Delta t')$	$x(\Delta t')$	$f_{VAc}(t)$	$F_{VAc}(\Delta t')$	$x(\Delta t')$
0.8333	0.6788	0.0537	0.8973	0.7451	0.1235
0.8333	0.6804	0.1171	0.8973	0.7406	0.1468
0.8346	0.6374	0.0232	0.8973	0.7363	0.1645
0.8346	0.6566	0.0405	0.9025	0.7485	0.0950
0.8346	0.6721	0.1048	0.9025	0.7421	0.1191
0.8346	0.6783	0.1356	0.9079	0.7556	0.0393
0.8393	0.6820	0.0835	0.9079	0.7622	0.1010
0.8421	0.6818	0.0669	0.9079	0.7526	0.1195
0.8471	0.6548	0.0327	0.9079	0.7577	0.1447
0.8471	0.6772	0.0660	0.9079	0.7679	0.1756
0.8471	0.6970	0.1598	0.9141	0.7664	0.0642
0.8471	0.6938	0.1830	0.9141	0.7511	0.0836
0.8643	0.6966	0.0927	0.9141	0.7585	0.1098
0.8643	0.7116	0.1309	0.9141	0.7715	0.1419
0.8696	0.7012	0.0954	0.9141	0.7763	0.1733
0.8696	0.7131	0.1276	0.9187	0.7698	0.1400
0.8696	0.7193	0.1556	0.9242	0.7758	0.0830
0.8696	0.7216	0.1822	0.9242	0.7822	0.1165
0.8757	0.7238	0.1749	0.9289	0.7818	0.0286
0.8814	0.7335	0.1515	0.9289	0.7998	0.0979
0.8814	0.7375	0.1848	0.9289	0.7927	0.1468
0.8873	0.7280	0.1142	0.9289	0.8078	0.1736
0.8873	0.7344	0.1490	0.9333	0.8129	0.1492
0.8873	0.7461	0.1819	0.9333	0.8180	0.1761
0.8925	0.7189	0.0815	0.9376	0.7980	0.0366
0.8925	0.7302	0.1175	0.9376	0.8119	0.1174
0.8925	0.7457	0.1516	0.9376	0.8185	0.1453
0.8925	0.7419	0.1742	0.9430	0.8182	0.0839
0.8973	0.7354	0.0315	0.9430	0.8254	0.1128
0.8973	0.7236	0.0883			