JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Effects of Shear Rate, Temperature, and Polymer Composition on the Shear Stress of Polyethersulfone/1-Methyl-2-pyrrolidone Cast Solutions

Nayef M. Ghasem* and Mohamed H. Al-Marzouqi

Department of Chemical and Petroleum Engineering, United Arab Emirates University, Al-Ain, P.O. Box 17555, United Arab Emirates

ABSTRACT: Polyethersulfone (PES) is extensively used for the preparation of hollow fiber membrane contactors; these modules are utilized in microfiltration (MF), ultrafiltration (UF), and gas separation. Viscosity plays a crucial role in the fabrication of hollow fiber membranes and their separation performance. In this study the effect shear rate, temperature, and polymer composition on shear stress of dope solutions prepared from PES polymer, dissolved in 1-methyl-2-pyrrolidone (NMP) solvent, is experimentally investigated. An empirical equation is developed to describe these effects on the shear stress of the polymer solutions. Data were obtained for (0.050, 0.10, 0.15, 0.20, and 0.25) mass fractions of PES polymer in NMP solvent at temperatures for (298, 308, 318, 328, 338, and 353) K. The shear stress results calculated by the developed equation describe well the set of experimental data.

INTRODUCTION

Viscosity is an essential property which plays a significant function in fluid transportation, mixing, heat transfer, or mass transfer operations. Polymer solution viscosities at different temperatures are also important in polymer extruding and fabrication of polymeric hollow fiber membranes used in dialysis, water treatment, and gas separation processes. Fluids are classified based on their performance into Newtonian and non-Newtonian. Newtonian fluids are defined as those exhibiting a direct proportionality relationship between shear stress and shear rate, whereas for non-Newtonian fluids, the relationship between shear stress and shear rate is not linear. Pseudoplastic fluids are called shear thinning fluids, because their apparent viscosity decreases with shear rate; hence, increased shearing breaks down the internal structure within the fluid rapidly.[1]

The viscosity of polyisoimide solutions was studied by Levinson et al.;[1] two models were developed, to describe the effect of temperatures and shear rates on the viscosity. The data were obtained for various polyisoimide solutions prepared in different ratios of oxolane/diglyme in 1-methyl-2-pyrrolidone (NMP), and the viscosity of the polymer solutions was tested at various temperatures. These models account for temperature dependencies in the power law shear-thinning exponent. Experimental data were found to fit the proposed model reasonably well. The effects of polymer concentration, temperature, and surfactant on the rheological properties of poly(*n*-isopropylacrylamide), poly(NIPAM), were studied by Tam et al.;[2] the investigators found that there do exit unusual rheological behavior for the effect of viscosity as a function of temperature which was elucidated to the phase behavior of the polymer. Benchabane and Bekkour[3] measured the critical concentrations of sodium carboxymethyl cellulose (CMC) with a rotational rheometer, and they observed that above a critical shear rate all CMC solutions exhibited shear thinning behavior and all of the flow curves were described by the cross model. The characterization of CMC solutions was completed with a time-dependent viscosity that showed that CMC solutions exhibit strong thixotropic behavior, mainly at high CMC concentrations. The influences of shear rate on relative viscosity of different polymer ratios of carboxymethyl cellulose and κ-carrageenan in aqueous solution were examined by Gómez-Díaz et al.,[4] and the effect of temperatures on rheological behavior of the solution was investigated.

Table 1. Statistics Used to Compare Shear Stress Calculated from eq 1 and Experimental Data

AAD %	1.2
BIAS	−5.1
SDV	11
rms	0.12

Table 2. Estimated Parameters of eq 1

parameter	estimated value	asymptotic standard error (ASE)	Wald 95 % confidence interval lower	Wald 95 % confidence interval upper
A/Pa	2.2	0.012	2.2	2.3
B/s^{-1}	18000	120	18000	19000
C/K	1500	5.2	1500	1600
D	0.28	0.021	0.28	0.29
m	1.3	0.013	1.3	1.3

Special Issue: Kenneth N. Marsh Festschrift

Received: March 29, 2011
Accepted: May 18, 2011
Published: May 25, 2011

Table 3. Shear Stress, τ, versus Shear Rate, $\dot{\gamma}$, at Different Temperatures and PES Mass Fractions

		τ/Pa					
100W	$\dot{\gamma}$/s^{-1}	298 K	333 K	318 K	328 K	338 K	353 K
25	0.3	105	85	64	49	42	30
	0.7	182	162	125	97.6	80.6	60
	1	250	231	178	141	116	87
	1.4	330	293	228	182	152	114
	1.7	390	353	276	222	185	139
	2.1	450	409	323	261	218	165
	2.4	500	464	368	298	249	189
	2.8	560	516	410	333	279	212
	3.1	620	569	450	367	307	234
	3.5	666	613	489	400	336	256
	3.8	717	658	527	433	364	278
	4.1	768	702	564	464	391	300
	4.5	817	744	600	495	416	321
	4.8	867	785	634	525	442	341
	5.2	916	824	668	554	467	361
	5.5	963	862	701	583	492	382
	5.9	1010	900	733	611	516	401
	6.2	1060	936	764	638	539	420
	6.6	1090	971	794	665	562	440
	6.9	1140	1010	825	690	585	457
	7.2	1180	1040	854	717	607	476
	7.6	1220	1070	883	742	629	494
	7.9	1270	1100	911	768	650	513
	8.3	1325	1130	938	792	672	530
	8.6	1368	1160	966	816	692	547
	9	1411	1190	1006	839	713	564
	9.3	1454	1220	1035	863	730	581
	9.7	1496	1240	1066	887	752	597
	10	1520	1290	1096	909	772	613
20	2	87	71	56	44	36	27
	3	164	135	108	87	72	54
	5	234	194	156	126	105	79
	7	297	248	201	164	137	104
	9	356	299	243	199	167	127
	10	412	347	284	234	197	150
	12	464	393	322	266	225	172
	14	514	436	359	298	251	194
	16	562	478	394	329	278	215
	17	608	519	429	358	303	235
	19	651	558	462	387	328	255
	21	694	596	494	415	351	274
	22	734	632	525	442	375	294
	24	773	667	556	469	398	312
	26	811	701	585	495	420	330
	28	848	734	614	520	441	348
	29	884	767	642	545	463	366
	31	918	798	669	570	483	383
	33	952	829	696	594	504	400
	35	985	859	722	617	524	417
	36	1020	888	748	640	544	433
	38	1050	917	773	662	563	449
	40	1095	945	797	684	581	465
	41	1132	972	821	706	600	481
	43	1170	998	845	727	618	496
	45	1203	1020	868	748	636	511
	47	1242	1050	890	769	654	526
	48	1275	1070	913	789	671	541
	50	1313	1100	934	809	688	556
15	35	238	200	170	145	127	104
	69	400	344	293	251	218	176
	104	560	474	404	345	300	240
	138	700	593	504	431	374	302
	172	830	704	602	514	446	366
	207	960	815	692	593	514	421
	241	1080	918	780	669	580	472
	276	1200	1022	867	744	644	527
	310	1300	1110	940	800	704	578
	345	1400	1210	1025	870	766	620
	379	1530	1300	1110	940	820	670
	409	1600	1380	1150	1000	870	700
10	35	51	41	35	29	25	17
	69	95	78	66.7	55.6	48	34.2
	104	135	112	96.1	80.9	70	50.5
	138	171	142	123	104	90	66.3
	172	204	171	149	127	110	81.6
	207	235	199	173	148	128	95.8
	241	265	224	196	169	146	110
	276	293	248	218	188	163	123
	310	319	272	240	207	179	137
	345	344	294	260	225	195	150
	379	368	316	279	242	211	162
	414	392	336	298	259	226	175
	448	414	356	317	276	242	187
	483	445	376	334	292	256	198
	517	465	395	352	308	270	210
	552	485	413	369	323	285	221
	586	510	431	385	338	299	233
	621	530	449	401	353	312	244
	655	560	465	417	367	325	255
	690	580	490	432	381	339	266
	724	610	510	447	395	352	276
	759	630	530	462	408	365	287
	793	650	544	476	421	378	297
	828	680	560	491	435	391	308
	862	700	580	505	447	404	318
	897	720	600	518	460	416	328
	931	740	620	532	473	429	339
	966	760	640	545	485	442	349
	1000	780	660	558	497	454	359
5	35	9	6	5	4	4	3
	69	17	14	11	9	8	6
	104	25	20	16	13	12	10
	138	32	26	22	17	15	12
	173	39	32	27	21	19	15

Table 3. Continued

		τ/Pa					
100*W*	$\dot{\gamma}$/s^{-1}	298 K	333 K	318 K	328 K	338 K	353 K
	207	47	38	32	25	23	18
	241	54	44	37	29	26	21
	276	62	50	42	33	30	24
	310	69	56	47	37	34	27
	345	76	62	52	41	37	30
	379	83	68	57	45	41	33
	414	90	73	61	49	45	36
	448	96	79	66	53	48	39
	483	103	85	71	57	52	42
	517	110	90	76	61	55	45
	552	116	96	81	65	59	48
	586	123	101	85	69	62	50
	621	130	107	90	73	66	53
	655	136	113	95	76	69	56
	690	142	118	100	80	73	59
	724	149	124	105	84	76	62
	759	155	129	109	88	80	65
	793	161	134	114	92	83	68
	828	167	140	118	95	87	71
	862	173	145	123	99	90	73
	897	180	150	128	103	94	76
	931	185	155	132	107	97	79
	966	192	161	137	111	101	82
	1000	197	166	141	114	104	85

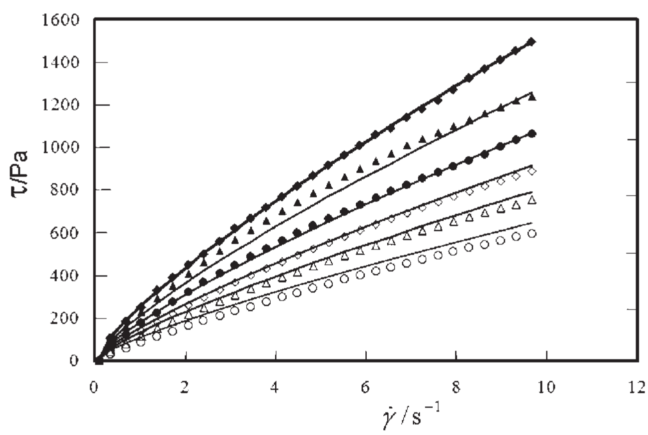

Figure 1. Shear stress versus shear rate at various temperatures, 0.25 mass fractions PES. Solid lines are calculated values. ♦, 298 K; ▲, 308 K; ●, 318 K; ◊, 328 K; △, 338 K; ○, 353 K.

Models based on the viscosity of individual polymer solutions were engaged to check up the experimental data.

In general, viscosity is an essential factor in the fabrication of polymeric hollow fiber membranes. Among these polymers, polyethersulfone (PES) is widely used for the preparation of microfiltration (MF), ultrafiltration (UF), and gas separation hollow fiber and flat sheet membranes. PES hollow fiber membranes are promising technology for water treatment and removal of pollutant gases such as CO_2 and H_2S from natural gas and flue gas. Membrane ultra filtration is

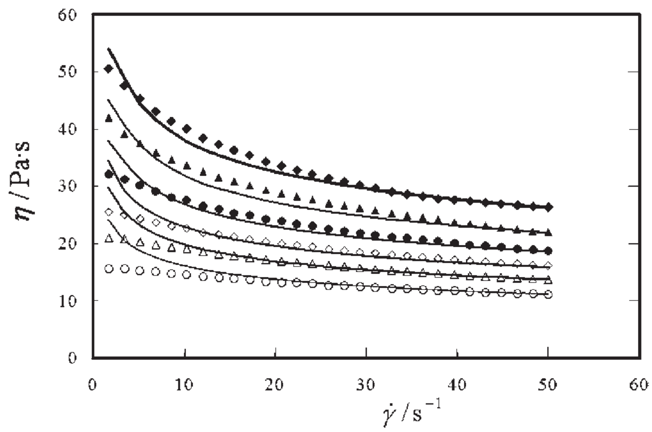

Figure 2. Viscosity versus shear rate at various temperatures, 0.20 mass fractions PES. Solid lines are calculated values. ♦, 298 K; ▲, 308 K; ●, 318 K; ◊, 328 K; △, 338 K; ○, 353 K.

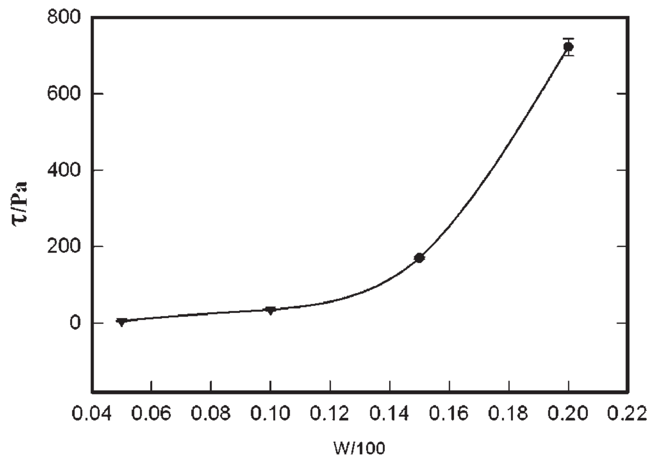

Figure 3. Shear stress versus PES mass fractions at 318 K and shear stress 35 s^{-1}. The solid line is the calculated values.

well-known as a capable technique in water purification process. Membrane filtrations are easy to operate in comparison with conventional water treatment methods, and the energy required for operation and maintenance is small. It is a talented technology for purification and production of drinking water. Membrane filtration methods are capable of disinfecting water and removing its turbidity at moderately low pressure. Another advantage of membrane filtrations are the capability of removing a broad range of substances, and the production of stable quality water.[5−11]

As viscosity is an important factor in the preparation of PES hollow fibers membranes, the aim of the present work is to experimentally study the effect of shear rate, temperature, and polymer compositions on shear stress and to develop a model equation capable to describe the effect of shear rate, temperature, and PES mass fraction on shear stress. The developed model equation can also be used to predict shear stress for polymer solutions at various PES mass fractions and temperatures that have not been experimentally studied and are within the correlation acceptable range. Various solutions of PES/NMP mass fractions (0.050, 0.10, 0.15, 0.20, and 0.25) are prepared and tested at various temperatures (298 to 353) K and variable shear rates.

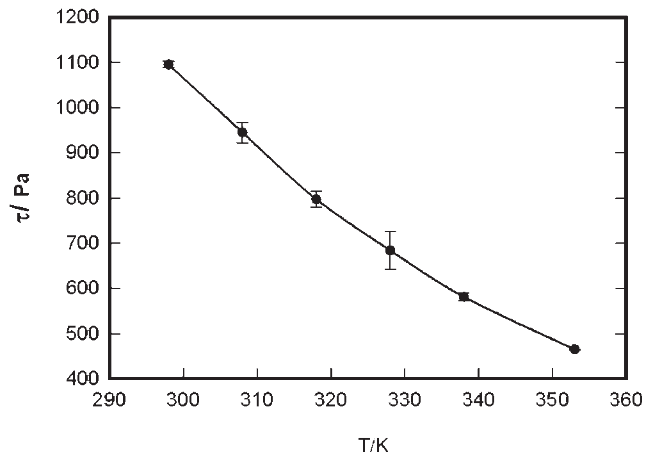

Figure 4. Shear stress versus temperature at fixed PES mass fraction, 0.20, and fixed shear rate, 35 s^{-1}.

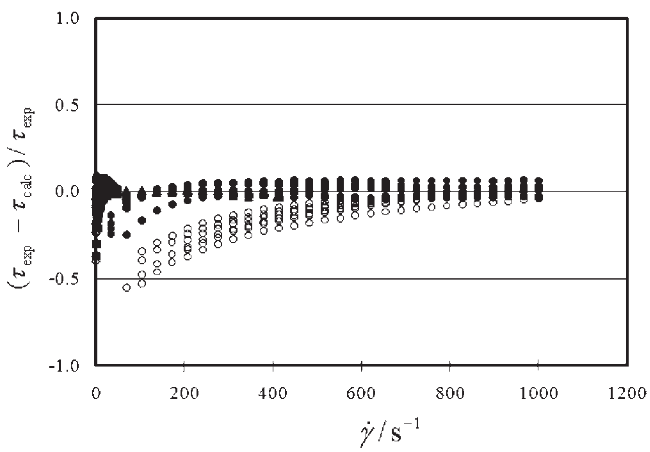

Figure 5. Fractional deviation between experimental (τ_{exp}) and calculated (τ_{calc}) shear stress versus shear rate for various PES mass fractions; ◇, 0.25; ■, 0.20; ▲, 0.15; ●, 0.10; ○, 0.05.

EXPERIMENTAL SECTION

PES (Ultrason E6020 P), with a weight-average molecular weight of 65 000, was purchased from BASF Company. The solvent, 1-methyl-2-pyrrolidone (purity 0.99 mass fraction), was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Ultrason pellets can absorb moisture very rapidly and must be dried before processing. Vacuum or dry air oven operating at (403 to 423) K is recommended. Circulating air ovens are unsuitable. Drying time is dependent on moisture level, but the materials must be dried at least four hours. Five different concentrations of PES/NMP were prepared: (0.05, 0.10, 0.15, 0.20, and 0.25) mass fraction PES. Each solution was mixed for 24 h using magnetic stirrer to ensure the solutions are homogeneous and perfectly mixed. The rotational viscometer, Rheolab QC, from Anton Paar, Austria [maximum torque of 50 mN·m, torque resolution of 0.01 mN·m, speed (0.6 to 90000) s^{-1}, shear stress range of (0.25 to 75) mN·m, shear rate range of (10^{-2} to 4000) s^{-1}, viscosity measuring range of (1 to 10^9) mPa·s] is used for the shear stress measurements. In this instrument, the viscous torque on a spinning object is monitored by measuring the rotation frequency of the object. This is converted directly into a viscosity by the software of the instrument and reported on the screen. The device was used to measure the shear stress of the polymer solutions versus shear rate for temperatures in the range (298 to 353) K; the same range of temperatures is used in the preparation of polymeric hollow fiber membrane utilizing nonsolvent-induced face separation techniques.

Correlation Development. Most of the equations which describe the relationship between the shear stress and shear rate are empirical correlations. The two-parameter power-law models ($\tau = K\dot{\gamma}^n$) are the most commonly used as an empirical equation for pseudoplastic fluids. The power law model is a useful rheological model that describes the relationship between viscosity or shear stress and shear rate in a specific range of shear rates where shear thinning occurs in a non-Newtonian fluid. The power law is accurate for the prediction of viscosity at various shear rates for molten polymers.[12] The applicability of the power law gets better with the raise of solution concentrations. If n is equal to 1, the flow is Newtonian, and the viscosity does not change with shear rate. The flow is pseudoplastic or shear thinning if n is less than 1. Most polymer melts and solutions are pseudoplastic. The flow is dilatant or shear-thickening if n is greater than 1. The Andrade equation describes the temperature reliance of liquid viscosities.[13] In the present work, a more comprehensive model adopted from the parabolic shape is used in fitting the experimental data.[14,15]

$$\tau = A[(1 + B^{-1}\dot{\gamma})^m - 1]^{m^{-1}} e^{CT^{-1}} e^{D(100W)} \qquad (1)$$

where τ/Pa is the shear stress, $\dot{\gamma}$/s^{-1} is the shear rate, and A/Pa, B/s^{-1}, C/K, D, and m are empirical parameters. T/K is the temperature, and W is the mass fraction of PES in NMP.

In this correlation m is just a fitting parameter and is different than n in the power low model. The empirical parameters are obtained by fitting the experimental data with the proposed model. The statistics used to compare shear stress calculated using eq 1 to experimental shear stress can be found elseware.[16]

High values of the average absolute deviation (AAD) and BIAS indicate systematic differences between experimental data and calculated results. Values of the standard deviation (SDV) give an indication of the systematic or random dispersion of the data set about the BIAS value. The rms provides another indication of the systematic or random dispersion of the data from the developed equation. Data sets are accurately represented by the developed correlation when all four statistical parameters are near zero.

The fitted empirical constants were calculated using Easy-Fit software package.[17,18] The statistics was used to compare shear stress calculated from eq 1 and experimental data shown in Table 3. The estimated parameters were within the 95 % confident interval lower and upper limits. The obtained R^2 values were relatively high (above 0.99). The AAD, SDV, BIAS, and root-mean-square (rms) were calculated and are shown in Table 1. As close the |Bias| is to the rms, the bigger are the systematic deviations. Bias = 0 means that there are not systematic deviations. As Bias is more or less the half of the rms, the systematic deviations are of the same magnitude than the random deviations. Estimated values of ADD, SDV, BIAS, and rms are not very close to zero which indicates that there is a systematic deviation. Figure 5 shows that the systematic deviations are quite important mainly for low PES mass fractions of 0.05. The parameters of eq 1 are shown in Table 2. The experimental data at various shear rates, temperature, and PES compositions are shown in Table 3.

RESULTS AND DISCUSSION

Figure 1 shows the effect of shear stress versus shear rate for 0.25 PES mass fractions in NMP solvent at five different temperatures: (298, 308, 318, 328, 338, and 353) K. The figure demonstrates that, as shear rate increases, shear stress increases accordingly at any of those temperatures. At a specific value of shear rate, the shear stress was found to increase exponentially as polymer mass fraction increases, because, the polymer solution becomes thicker when the amount of polymer added to a fixed volume of solvent, increases. Calculated values were close to the experimental data at high values of shear rates; by contrast, at low shear rates there is significant deviation. The effect of solution viscosity of 0.2 mass fractions PES at variable shear rates and five different temperatures is depicted in Figure 2. The figure revealed how the viscosity is affected with changes in shear rate, temperature, and polymer compositions; at high shear rates the change in viscosity is very insignificant. At fixed values of shear rate, the viscosity decreases as temperature increases.

The effect of polymer mass fraction on shear stress at a fixed temperature (308 K) and fixed shear rate (35 s^{-1}) is revealed in Figure 3. The figure exemplifies the exponential relationship between shear stress and polymer mass fractions. This backs up the exponential relationship between shear stress and polymer mass fraction used in eq 1. The shear stress increased sharply for solutions with mass fractions higher than 0.15. This confirmed the suitable range of PES mass fraction in dope solutions used in the fabrication of polymeric hollow fiber membranes (the PES/NMP suitable range is between 0.15 and 0.25 mass fractions of PES). The effect of temperature on shear stress is depicted in Figure 4; the figure demonstrates that shear stress decreases as temperature increases. This agreed with the inverse relationship between shear stress and temperature used in eq 1. At low PES mass fractions, polymer solution shows evidence of Newtonian behavior fluid. The fractional deviation between experimental and calculated shear stress versus shear rate is shown in Figure 5. The plot shows that the deviation between calculated and experimental values is considerable at the low shear rates (less than 200 s^{-1}) and for a PES mass fraction of 0.05. By contrast, the discrepancy decreases with increasing shear rates and higher values of PES mass fractions.

CONCLUSIONS

A generalized model equation was developed to depict shear stress as a function of shear rate, temperature, and polymer mass fractions for PES/NMP polymer solutions. The polymeric solution is frequently used in the fabrication of hollow fiber membrane using nonsolvent-induced phase separation (NIPS) techniques. The generated correlation successfully describes shear stress to the shear rate for shear rate range (0 to 1000) s^{-1}, and PES mass fractions range from (0.05 to 0.25). The PES/NMP polymeric solution behaves as pseudoplastic fluids, the shear stress increases as shear rate increases, and polymer mass fractions in the dope solution increases. The developed equation is reliable to predict shear stress at various shear rates, temperature, and polymer mass fraction for values other than existing data.

AUTHOR INFORMATION

Corresponding Author

*E-mail: nayef@uaeu.ac.ae.

Funding Sources

The authors would like to acknowledge the financial support provided by the Japan Cooperation Center, Petroleum (JCCP) and the technical support of the JX Nippon Research Institute, Ltd. They would also like to thank ADGAS and UAE University Research Affairs for their support.

REFERENCES

(1) Levinson, W.; Czornyj, G.; Capo, D.; McMahon, J. Effect of temperature and shear rate on polyisoimide solution viscosity. *Polym. Eng. Sci.* **2004**, *18*, 1221–1225.

(2) Tam, K. C.; Wu, X. Y.; Pelton, R. H. Effect of Polymer Concentration, Temperature, and Surfactant on the Viscosity of Aqueous Solutions. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *31*, 963–969.

(3) Benchabane, A.; Bekkour, K. Rheological properties of carboxymethyl cellulose (CMC) solutions. *Colloid Polym. Sci.* **2008**, *286*, 1173–1180.

(4) Gómez-Díaz, D.; Navaza, J.; Quintáns-Riveiro, L. Influence of Mixing and Temperature on the Rheological Properties of Carboxymethyl Cellulose/κ-carrageenan Mixtures. *Eur. Food Res. Technol.* **2008**, *5*, 1397–1402.

(5) Atchariyawuta, S.; Jiraratananona, R.; Wang, R. Mass Transfer Study and Modeling of Gas−liquid Membrane Contacting Process by Multistage Cascade Model for CO_2 absorption. *Sep. Purif. Technol.* **2008**, *63*, 15–22.

(6) Dan-ying, Z.; You-yi, X.; Han-tao, Z. The Influence of PEG Molecular Weight on Morphologies and Properties of PVDF Asymmetric Membranes. *Chin. J. Polym. Sci.* **2008**, *26*, 405–414.

(7) Byoung, H. K.; Byoung, C. The Rheological Properties of the Solutions of PVDF in DMAc for Electrospinning. *Korean Fiber Soc.* **2004**, *41*, 419–423.

(8) Jermann, D.; Pronk, W.; Meylan, S.; Boller, M. Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production. *Water Res.* **2007**, *41*, 1713–1722.

(9) Madaeni, S. S. The application of membrane technology for water disinfection. *Water Res.* **1999**, *33*, 301–308.

(10) Pearce, G. Introduction to membranes: Filtration for water and wastewater treatment. *Filtr. Sep.* **2007**, *44*, 24–27.

(11) Haiyang, Y.; Hao, L.; Zhu, P.; Yan, Y.; Zhu, Q.; Chenggao, F. A novel method for determining the viscosity of polymer solution. *Polym. Test.* **2004**, *23*, 997–901.

(12) Rodríguez, F. *Principles of Polymer Systems*; McGraw-Hill: New York, 1970.

(13) Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, C. F. *Dynamics of Polymeric Liquids*; John Wiley & Sons: New York, 1977.

(14) Ghasem, N. M.; Marzouqi, M.; Elnaas, M. Effect of Temperature, Composition, and Shear Rate on poly-1,1-difluoroethene/*N,N*-dimethylacetamide Solution Viscosity. *J. Chem. Eng. Data* **2009**, *54*, 3276–3280.

(15) Murrell, H. N.; Boucher, E. A. *Properties of Liquids and Solutions*; John Wiley & Sons: New York, 1982.

(16) Kittel, P. *Advanced in cryogenic engineering*, Vol. 39A; Plenum Press: New York, 1994.

(17) Alzahrani, S. M. A generalized rheological model for shear thinning fluids. *J. Pet. Sci. Eng.* **1997**, *17*, 211–215.

(18) Schittkowski, K. *EASY-FIT User Guide*; Department of Mathematics, University of Bayreuth, Germany, 2008.